



A new indexing approach for evaluating heavy metal contamination in groundwater

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HIGHLIGHTS

- Evaluated conventionally used indices: heavy metal pollution index, contamination index and heavy metal evaluation index.
- Developed of a new indexing approach, heavy metal contamination index (HCI), with a set of six distinct water classes.
- Assigned weightage to heavy metal parameters through Delphi's method for computing HCI.
- Applied chemometric techniques for distinguishing various sources of heavy metal contamination.
- Integrated HCI with cluster analysis for verifying possible factors and extent of groundwater contamination.

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ABSTRACT

Three indexing methods, namely heavy metal pollution index (HPI), contamination index (C_d) and heavy metal evaluation index (HEI), are commonly used for heavy metal evaluation in groundwater. These methods have several limitations. In HPI, 14 out of 15 groundwater samples collected in the study area of Nalagarh valley, Himachal Pradesh, India qualify for drinking purposes with their values varying between 10.73 and 107.50 (critical limit = 100), while in C_d , the same number of samples (>90%) are rejected as their values ($C_d = 1.31-37.87$) exceed the critical limit of 3. HEI varies from 10.31 to 46.87 with a mean of 26.06, but since it does not have a defined critical limit, quality assessment depends on worker's discretion. It thus becomes very confusing as to which indexing method to use. To overcome this dilemma, a very simple indexing method called 'heavy metal contamination index (HCI)' has been developed on the basis of assigning weight to each heavy metal parameter. A new classification system with six distinct water classes of different uses too has been proposed considering the regulatory limits, human health risk and toxicity of the violator parameters. Regression analysis confirms that HCI has larger number of significantly correlated key parameters compared to the other three indices. Chemometric techniques confirm that Cr, Cu, Fe, Mn and Zn are derived from lithogenic inputs and As, Cd, Ni and Pb from anthropogenic sources. HCI when integrated with Cluster Analysis gives the best possible results in identifying factors that influence the various water classes.

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1. Introduction

Methods of integrating numerous water quality variables in a specific index to assess contamination levels have found wide-spread uses in environmental science and engineering. Various pollution indices, namely heavy metal pollution index (HPI),

contamination index (C_d) and heavy metal evaluation index (HEI), have been used in the past to evaluate the extent of pollution in groundwater (Mohan et al., 1996; Backman et al., 1997; Prasad and Bose, 2001; Edet and Offiong, 2002; Mustafa, 2008; Prasanna et al., 2012; Venkatramanan et al., 2015; Singh et al., 2017; Wagh et al., 2018). Multivariate chemometric techniques that include principal component analysis (PCA) and cluster analysis (CA) are purposefully used to overcome the limitations of these pollution indices (Lumb et al., 2011; Singh et al., 2014; Herojeet et al., 2016). These chemometric analytical techniques are considered

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trustworthy and credible approaches for elucidation of complex data matrices to distinguish between the anthropogenic and natural sources of pollution in groundwater (Okiongbo and Douglas, 2015; Herojeet et al., 2015; Jacintha et al., 2016; Esmaeili et al., 2018).

A brief review of these geochemical indexing approaches historically used by various workers is necessary in terms of their usability and correctness. This contribution tries to apply these traditionally used indices in appraising the contamination level of groundwater in heavy metals in a strategically located industrial area in the foothills of the Himalayas in the northwestern State of Himachal Pradesh, India (Fig. 1), discusses their limitations and proposes a new easy-to-use indexing approach that does better assessment of heavy metal contamination. Also, it proposes a new

classification system that assigns water samples to six distinct water classes depending on their applicability. Chemometric techniques have been used to distinguish between the probable sources of heavy metals in groundwater and integrate the newly proposed method with cluster analysis in order to identify factors that influence the water classes.

Foothill zones of the lesser Himalayas due to their geological and physiographic settings act as the key aquifer recharge areas for the regions in the south. Therefore, it is essential that the water resources of these foothill zones be preserved as much as possible from contamination. In fact, better pollution indices are needed to manage this important recharge area so that industry can advance without degrading the water resources. The results of this work, therefore, shall be an eye opener not only for the Indian State of

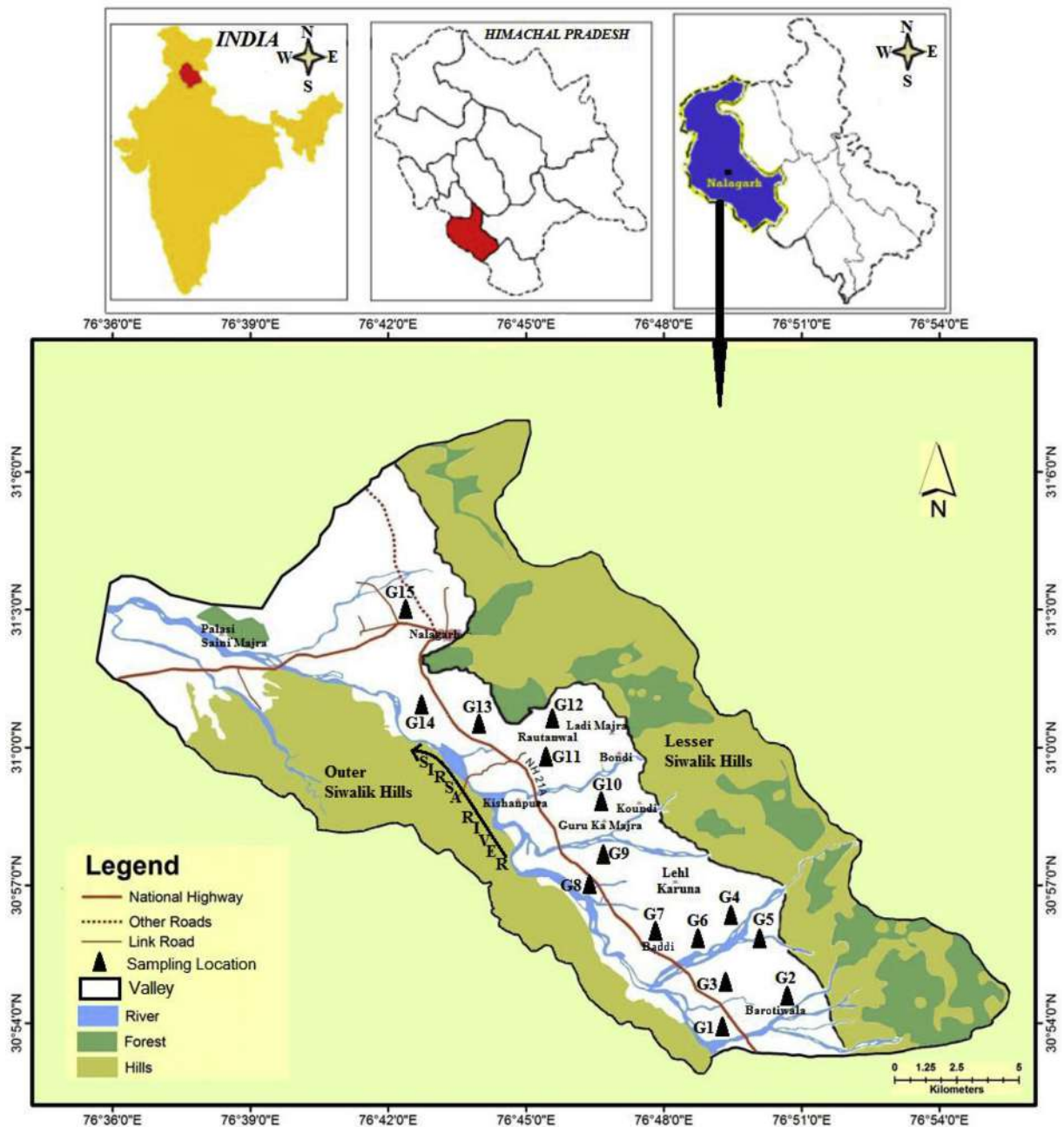


Fig. 1. Location of the Nalagarh valley, Himachal Pradesh, India.

Himachal Pradesh but also for similar other areas across India and elsewhere to take suitable measures for striking a fine balance between environmental sanctity and industrial advancement.

2. Materials and methods

2.1. Study area

Nalagarh, a narrow intermontane valley, with geographical size of about 250 km² in Himachal Pradesh, India is taken as the study area for comparison of the conventionally used indexing approaches (Fig. 1). Himachal Pradesh is a sub-Himalayan hilly State with strong focus on industrialization in recent years. Nalagarh valley has the highest concentration (~70%) of both large scale and medium scale industries in the State (GoHP, 2012). The designated region for industrial development in Nalagarh valley is commonly known as the Baddi-Barotiwala-Nalagarh (BBN) Industrial Belt (Herojeet et al., 2013) where about 12 different categories of industries are situated (Table 1). There also are numerous open-cast mining operations active in the area for quarrying limestone, minerals and stones, riverbed boulders and sand. In recent years, many industries from the neighboring and southern States have shifted to Nalagarh valley due to popular subsidies granted by the Himachal Pradesh State Government. Many fertile agricultural lands are being rapidly converted to industrial areas causing an environmental chaos (GoI, 2012). About 55% of industrial units do not possess valid legal industrial permits (Anonymous, 2014). As per a report prepared by the BBN Authority in 2007, about 72% of

industrial units are operating in BBN without Effluent Treatment Plants (ETP) making the groundwater resources more vulnerable to pollution (Kamaldeep et al., 2011). A detailed account of the environmental status in Nalagarh valley has been given by Rajkumar et al. (2019). This report presents an assessment of the pollution menaces in the groundwaters of the Nalagarh valley, and critically examines the various pollution indices that have been conventionally used historically. Also, it proposes a new indexing method that not only satisfies the limitations of these indices but also classifies the collected water samples into various water classes depending on their usability for domestic purposes.

2.2. Sampling and analysis

Groundwater samples were collected in May 2014 from 15 different sampling locations of Nalagarh valley (Fig. 1). Samples were collected in good quality (HDP) plastic bottles (1000 ml) with cover lock using Whatman filter paper no. 42 (to remove suspended particles) after pumping for about 10 min to obtain fresh samples. For the analysis of metal constituents, the samples were acidified with HNO₃ to maintain pH ~2 in the field. They were then preserved in laboratory at 4 °C until their analysis. Each of these groundwater samples (50 ml) was digested with 5 ml of concentrated HNO₃ at 80 °C until its volume reduced to 20 ml on electric hot plate (Johnson Delite Company, India). Further, concentrated HNO₃ (5 ml) was added and then heated for another 10 min or until the solution appeared transparent (APHA, 1985). Whatman filter paper with a diameter of 125 mm and pore size of 2.5 μm was used to

Table 1

List of important industrial units in the Nalagarh valley, Himachal Pradesh, India (after GoHP, 2011).

S. No.	Category of industrial manufacturing units	No. of Units	Manufacturing products	Nature of effluents/wastes
1.	Automobile/engineering/tool rooms/fabrications	81	Auto and tractor parts, railway products, air and oil filters, grinder wheels, panel building and fabricating.	Acids, phenols, cyanogens, low pH, alkalies, limestone, oil, fine suspended solids, cyanides, cyanates, iron salt, ores and coke.
2.	Chemicals/acids/gasses/fire equipment/powder coating	37	Fuel additives, wood adhesives, aromatics and flavours and textile chemicals.	Toxic compounds, phenols, high acidity and alkalinity.
3.	Cosmetics/soap/washing items/perfumes	58	Soaps and detergents, handwash lotions, facial kits, perfumes and deodorants, mosquito killers.	High BOD, tetra propylene derived alkynes and benzene sulphonate.
4.	Electrical & electronics/Home appliances	121	Batteries, inverters, air conditioners, transformers, CFL lamps, printer circuit boards, DVDs and VCDs, electrical appliances and accessories.	Heavy metals such as Cd, Ni, Zn, Pb, plastics and organic compounds such as polychlorinated biphenyls, polybrominated biphenyls, polybrominated diphenyl ethers and oils.
5.	Food/bakery/beverages/mineral water	39	Mineral waters, sweet confectionaries, liquor wines, sharbat and juices, food and beverage products.	High dissolved solids containing nitrogen, fermented starches and allied products.
6.	Sanitary/hardware/paints/furniture products	27	Plyboards, powder coating, paints, primers distempers, bathroom fittings and laminates mica.	Organic and inorganic reducing agents, silver and alkalies.
7.	Leather/footwear	20	Footwears, leather bags, mattresses, moulded insoles, leather watches and strips.	Cd, Cr, highly salted materials, coloured, dissolved and suspended matters.
8.	Pharmaceuticals/pesticides/ayurvedic medicines	258	Pharmaceutical products, pesticide products, x-ray machines, eye drops and ayurvedic medicines.	Aromatic compounds, highly suspended and dissolved organic matters such as vitamins, high acidity or alkalinity.
9.	Plastic/polymer/rubber/injection moulding	118	PVC pipes, plastic bottles, injection moulding, poly films, HDPE containers, rubber products and thermocoles.	Chlorides, suspended and dissolved solids, variable pH and high BOD.
10.	Printing & packing/paper products/stationery	178	Corrugated boxes, printing and packaging products, mono cartons, CFB foils, paper cones, photo copier machines and their assembling.	Suspended solids, high or low pH, colour, BOD, COD, high temperature and fibres.
11.	Steel & iron/TMT saria/ metal	47	Alloy and non-alloy steel materials, blisters, rounds, solder wires, brass wires, cadmium bronze wires, pipe fitting cisterns and sheet covers.	Toxic cyanides, Cd, Cr, Zn, Cu, Al and low pH.
12.	Textile/yarn/readymade garments/clothes	38	Readymade garments, polyester staple fibers, cotton fibers and yarn knitting.	Na, organic matter, colour, high pH and fibres.

Source: GoHP, 2011; Kaur, 2014

filter the digested solution. The solution was then quantitatively transferred to 50 ml volumetric flask by adding distilled water.

Measures were taken to prevent contamination and enhance confidence of data for bias and variability. All apparatus and glassware were washed for 24 h with 10% HCl and rinsed twice with double deionized water. The chemical solutions were prepared from Merck-GR grade chemicals and reagents using double deionized water. For calibrating instruments to obtain reliable results, bank samples were prepared from their stock solutions for each heavy metal parameter. The samples were analysed three times and instrumental calibration was done with drift samples for every 5 samples to ensure accuracy and efficiency for all metal analysis. The reference materials provided by the National Institute of Standards and Technology (RM 1643 E) were strictly followed. The uncertainty error was less than 10% for each heavy metal parameter analysed.

2.3. Integrated pollution indices for groundwater

The conventionally indexing approaches, namely HPI (Mohan et al., 1996), C_d (Backman et al., 1997), HEI (Edet and Offiong, 2002) and the newly proposed approach, 'heavy metal contamination index (HCl)', have been used to identify the heavy metal contamination level in groundwater in this study.

2.3.1. Heavy metal pollution index (HPI)

The HPI model developed by Mohan et al. (1996) represents the composite influence of heavy metals on the total quality of water. This index establishes a rating or weightage (W_i) between 0 and 1 and is inversely proportional to the standard permissible value (S_i) of the corresponding parameter (Horton, 1965; Brown et al., 1970; Reddy, 1995; Mohan et al., 1996; Prasad and Kumari, 2008). HPI is calculated using the formulae:

$$HPI = \frac{\sum_{i=1}^n Q_i W_i}{\sum_{i=1}^n W_i} \quad (1)$$

where Q_i is the sub-index of the i th parameter, W_i is the unit weight of the i th parameter and n is the number of parameters considered. The critical pollution index is taken as 100 in this indexing approach (Prasad and Bose, 2001).

The first step involves computation of relative weight (W_i) for each metal parameter. Here, W_i is taken as the inverse of maximum/upper admissible concentrations (MAC), S_i is the maximum permissible limit and I_i is the ideal value for each parameters as adopted from Edet and Offiong (2002) (Table 2).

Table 2
Standard values for computation of pollution indices (after Edet and Offiong, 2002).

Parameters	W	S	I	MAC
As	0.02	50	10	50
Cd	0.37	5	3	3
Cr	0.02	50	50	50
Cu	0.001	1000	2000	1000
Fe	0.006	300	200	200
Mn	0.02	100	500	50
Ni	0.05	20	20	20
Pb	0.75	100	10	1.5
Zn	0.0002	5000	3000	5000

Abbreviations.

W = weightage (K/MAC).

S = Standard permissible limit in $\mu\text{g/L}$.

I = Highest permissible limit in $\mu\text{g/L}$.

MAC = Maximum admissible concentrations/upper permissible limit in $\mu\text{g/L}$.

$$W_i = K/MAC \quad (2)$$

where K (constant of proportionality) $1/\sum_{i=1}^n 1/MAC$

In the second step, the sub-index (Q_i) is calculated for each heavy metal using Eq. (3).

$$Q_i = 100 \times \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \quad (3)$$

where M_i = measured metal value in the i th sample, I_i = ideal value or desirable limit of the i th parameter, and S_i = standard permissible limit of the i th parameter. The numerator gives the numerical difference between the two values, but the algebraic sign (-) is ignored.

2.3.2. Contamination index (C_d)

The contamination index (C_d) provides the degree of contamination or cumulative effects of different quality parameters, which are considered harmful to domestic water (Backman et al., 1997). Therefore, C_d is the summation of all contamination factors that exceed the upper permissible values, as shown in Eq. (4).

$$C_d = \sum_{i=1}^n C_{fi} \quad (4)$$

where $C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$ represents contamination factor and C_{Ai} and C_{Ni} are analytical value and upper permissible concentrations of the i th component, respectively. The letter N denotes the 'normative value' and C_{Ni} is taken as MAC as given in Table 2. C_d values are generally classified into three categories: low ($C_d < 1$), medium ($C_d = 1-3$), and high ($C_d > 3$) depending on contamination level.

2.3.3. Heavy metal evaluation index (HEI)

The HEI method like the HPI gives the overall water quality status with respect to heavy metal contents (Edet and Offiong, 2002). It is computed as in Eq. (5):

$$HEI = \sum_{i=1}^n Hc_i / Hmac_i \quad (5)$$

where Hc_i is the measured value of the i th parameter and $Hmac_i$ is the maximum/upper admissible concentrations of the i th parameter. This index is useful for the interpretation of pollution level and is primarily used for easy calculation steps (Edet and Offiong, 2002; Prasanna et al., 2012).

2.3.4. Heavy metal contamination index (HCl)

There are certain limitations of the above three indexing approaches as detailed in supplementary (Suppl.) Table S1 (elaboration in Results and Discussion). To overcome these limitations, a new approach, HCl, has been developed for assessment of heavy metal contamination with partial modification of an existing equation developed by Tiwari and Mishra (1985), which is primarily meant for evaluation of water quality based on physico-chemical parameters such as pH, electrical conductivity, total dissolved solids, total hardness, major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (HCO_3^- , CO_3^{2-} , Cl^- , NO_3^- , F^- , SO_4^{2-}). The proposed HCl, on the other hand, is based on heavy metal parameters such as, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The modification and development processes of this index have been divided into four stages as described below.

2.3.4.1. Selection of water quality parameters. Water quality monitoring is essential for assessing its suitability for various usages such as drinking and irrigation (Thakur et al., 2016). Quality standards such as those developed by the World Health Organization (WHO 2017) and Bureau of Indian Standards (BIS, 2012) are used in India. But then, selection of chemical parameters for assessment depends on the worker's discretion depending on the pollution sources and types of contaminants expected in a study area. In the present study, on the basis of the industry types, manufacturing products and effluents generated (Table 1), nine heavy metal parameters As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn are considered for assessment based on their impact on human health (Suppl. Table S2). These nine parameters have been used for development of the proposed HCI and its sub-indices.

2.3.4.2. Assignment of weightage for selected parameters. Assignment of weightage on each selected parameter for the proposed index is designed based on certain factors such as classification of the parameter as essential (necessary for human diet) or non-essential element, its carcinogenicity, health implications (acute, chronic and long-term effects) and importance in water quality evaluation. Cr, Cu, Fe, Mn and Zn are essential trace elements required in tiny amount by human body (Suppl. Table S2), while As, Cd, Ni and Pb are not required in human diet. The excess amount or deficiency of essential elements and presence of non-essential elements may cause numerous malfunctions in human body. Weightage refers to the relative importance and response of the selected parameter in the final result of the proposed HCI. On the basis of Delphi studies carried out by various workers (Horton, 1965; Brown et al., 1971; Lumb et al., 2011; Mohebbi et al., 2013), weights range from 1 to 4 with the maximum weight of 4 assigned to the highly carcinogenic parameters such as, Cd, Cr, Ni and Pb. These weight values are important in water quality assessment and human health toxicity (Suppl. Table S2). The minimum weight of 1 is given to Fe since it does not play any significant role in water quality appraisal (Mohebbi et al., 2013). The weightage assigned to each selected parameter in this study is given in Suppl. Table S3.

2.3.4.3. Calculation of the proposed HCI. The equation by Tiwari and Mishra (1985) defines water quality index (WQI) conventionally used in quality classification of water. But, this equation is very complex and requires log table for calculation purpose.

$$\text{WQI} = \text{antilog} \frac{\sum_{i=1}^n W_i \log q_i}{\sum_{i=1}^n W_i} \quad (6)$$

where W_i = relative weight of the i th parameter, q_i = quality rating of the i th parameter.

The sub-index for each chemical parameter is solved in the following manners in WQI and HPI, respectively.

$$q_i = 100 \times \frac{\{V_a - V_i\}}{(V_s - V_i)}, \text{ and} \quad (7)$$

$$Q_i = 100 \times \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \quad (8)$$

where V_a or M_i = measured value of the i th parameter, V_s or S_i = its standard value, V_i = its ideal value, which is taken as 0 (zero) for major cations and anions, except for pH (= 7 or 7.5, ideal value) and DO (= 14.6, ideal value), and I_i = its desirable limit.

There are some problems with the WQI equation: (i) it is not very clear whether to consider the desirable or permissible or maximum acceptable limit of BIS or WHO or any other international standard as the standard value (V_s) for the i th parameter, (ii) ideal value (V_i) is taken as zero assuming the pure state or ideal state of water without contamination, but getting such a state of water is very unusual considering the dynamic nature of the environment, and (iii) the calculation process is very complex and not user-friendly due to frequent use of log tables.

Limitations have also been identified in HPI (Mohan et al., 1996) equation as follows. (i) Problem arises in the calculation of quality rating (Q_i) of the heavy metals on the basis of the latest BIS (2012) and WHO (2017) standards, where only permissible limits or maximum allowance limits of heavy metals, such as those of Ba, Fe, Cd, Cr, Pb, Hg, Ni, and Se, are provided while HPI actually requires desirable limit (I_i) as the ideal value, which cannot be zero. (ii) The algebraic sign (-) is ignored in the calculation of numerator value. This means, taking Mn as an example for which 100 $\mu\text{g/L}$ is the desirable limit, if there are two samples having Mn concentrations of 70 $\mu\text{g/L}$ and 130 $\mu\text{g/L}$ (measured parameter, M_i), then both samples will have the same HPI quality rating value since the difference of the measured parameter value (M_i) and desirable value (I_i) will be 30 $\mu\text{g/L}$ for both these samples (viz. $70-100 = -30$, but the minus symbol is neglected, so it becomes +30, and $130-100 = 30$) although the quality of the first sample with Mn = 70 $\mu\text{g/L}$ is much better than the second sample with Mn = 130 $\mu\text{g/L}$ (iii) The denominator of quality rating or sub-index of heavy metals is calculated by the difference of permissible limit and desirable limit, but many heavy metals (e.g. Ba, Fe, Cd, Cr, Pb, Hg, Ni, and Se) do not have desirable limits thus leading to inaccuracy in HPI index calculation.

The expression of quality rating or sub-index (q_i or Q_i) in both WQI and HPI adds to a lot of confusion amongst the researchers. Since the ideal values (V_i) of cation and anion parameters are zero in the calculation of sub-index for WQI, the expression does not add significant value to the equation and its final result. The calculation of HPI becomes difficult and biased due to the absence of desirable limit of the metals since the latest water quality standards of BIS (2012) and WHO (2017) as well as other international water standards provide only maximum acceptable limits (permissible limits) for many heavy metals, such as Ba, Fe, Cd, Cr, Pb, Hg, Ni, and Se. Thus, use of WQI and HPI becomes highly restricted.

In order to simplify the equations, therefore, in the proposed HCI method, we have removed the ideal value or desirable value (V_i or I_i) expression because it is biased and is not a valid assessment of water quality. HCI is calculated using the following steps.

First, the unit weight (W_i) of each of the nine parameters (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) is computed by dividing the assigned weightage by its relative weight using the following formula (9):

$$W_i = \frac{Aw_i}{\sum_{i=1}^n Aw_i} \quad (9)$$

where W_i = relative weight of the input parameter, Aw_i = assigned weight of the input parameter, n = number of parameters. Suppl. Table S3 gives the international standards (Edet and Offiong, 2002), assigned weights of individual parameters and calculated unit weights (W_i).

The quality rating (q_i) scale of a selected parameter in each water sample is calculated by dividing its concentrations by its respective permissible limit and multiplying the results by 100 using Eq. (10)

$$q_i = \frac{C_i}{S_i} \times 100 \quad (10)$$

where q_i = the quality rating of a selected parameter, C_i = the concentrations of the selected parameter and S_i = its permissible limit. The summation of all unit weights of heavy metal parameters ($\sum_{i=1}^n W_i$), i.e., the denominator in the WQI equation, is always equal to 1 or approximates to 1. Therefore, the denominator component has been removed from the WQI equation in the proposed index (HCI).

Finally, for computing HCI, the metal sub-index (MI) is first determined for each parameter as in Eq. (11). The sum of MI values gives the heavy metal contamination index for each sample using Eq. (12).

$$MI_i = W_i \times q_i \quad (11)$$

$$HCI = \sum_{i=1}^n MI_i \quad (12)$$

where MI_i = the sub-index of the i th parameter, W_i = the unit weight of the i th parameter, q_i = the rating based on concentrations of the i th parameter and n = the number of parameters.

So, the proposed HCI method is different from WQI as well as HPI. In fact, HCI uses much simpler equations than those of WQI and HPI, and works very well for heavy metals appraisal even without the availability of desirable limits of some parameters such as Ba, Fe, Cd, Cr, Pb, Hg, Ni, and Se. HCI methods can be used to calculate all the heavy metal parameters by the permissible limits and maximum acceptable limits of both the latest and older versions of BIS and WHO water quality standards. Moreover, analyses in this work show that HCI is a superior index compared to others and is also well-supported by chemometric analyses. The essential differences between WQI and HCI are given in Suppl. Table S4.

2.3.4.4. Categorization of HCI water classes. The objective of developing water classes is to determine the actual quality status of different sampling locations. Normally, different water quality indices developed by various researchers categorize only five water classes for drinking purposes (Lumb et al., 2011). These types of classification consider only the water quality scale, such as excellent, good, poor, very poor and unfit, without considering the regulatory limits of concerned parameters, human health risk and toxicity of the violator parameters. The HCI water class has been developed so that the mean index value is considered as the threshold marker for development of water classes. Three equidistant division scales are marked above and below the HCI mean value to rank the water classes in agreement with the regulatory limits (Suppl. Table S5). Here, each measured parameter is purposefully compared with its standard limit to identify the violator parameter(s) in each water class and to assess its corresponding toxicity level. Groundwater samples with a greater number of deflected parameters in accordance with the regulatory limits will be of inferior quality and may pose serious threat to human health and vice versa. The adverse human health risks associated with each measured heavy metal parameters are discussed in Suppl. Table S2. Further, the toxicity risk of a single violator parameter on human health will be minimal as compared to the combined effect of multiple violator parameters in a water sample. The maximum value in the water-quality index has been kept at 100 for drinking purpose in this classification, so 0 indicates excellent water quality and 100 indicates poor water quality. Water

samples having HCI value above 100 are considered unfit for drinking. The proposed HCI classifies the water samples in six distinct classes namely excellent, good, marginal, poor, very poor and unfit as given Suppl. Table S5.

2.4. Chemometric analysis

Chemometric statistical techniques that include Principal Component Analysis (PCA) and Cluster Analysis (CA) have been effectively applied by many workers to extract the reliable sources of heavy metals in water (Yuan et al., 2014; Herojeet et al., 2015; Mehrabi et al., 2015). PCA is essentially used for reduction of large complex data matrices to provide meaningful information on the important parameters and better interpretation of variables (Singh et al., 2004, 2019; Herojeet et al., 2017). In the present study, prior to statistical analysis, all chemical parameters irrespective of their units were standardized (z-scale) individually with their mean values (zero) and standard deviations to get dimensionless values (Simeonov et al., 2004; Khanoranga and Khalid, 2019). Principal components (PCs) were extracted using varimax rotation method where the eigenvalues >1 is statistically accepted for interpreting results (Kaiser, 1960; Shrestha and Kazama, 2007). Cluster Analysis was used to classify a set of objects into similar groups (Wai et al., 2010). The clustering procedure was performed by Ward's linkage method (Otto, 1998) and similarity distance was measured by squared Euclidean distance on standardized raw data (z-transformation). The Sneath's test technique was used to determine the significance of cluster (Papazova and Simeonova, 2013). GIS software Mapinfo 6.5 and Vertical Mapper 3.0 were employed for spatial map preparation. A Microsoft Excel 2007 and Minitab 16 software were used for all data calculations and statistical analyses.

3. Results and Discussions

3.1. Groundwater conditions

The Nalagarh valley has a northwest-southeast (NW-SE) extension delimited by the river Sirsa on the south-west and the Siwalik Hills on the north-east. The geology of the area is very complex with a long history of tectonic activities (Khan, 1988). Stratigraphically, the Tertiary formations of the Siwaliks bound the valley and its flanks. Sandstones, quartzites, limestones, phyllites, slates and shales are the prominent rock types that are highly fractured along the faults and thrusts. Nalagarh thrust is a major fault marked by the two NW-SE trending tectonic zones. The Sirsa River flows along the Surajpur Fault (Khan, 1970). Groundwater in the valley occurs in pervious unconsolidated alluvial formations consisting of silt, sand, gravels, pebbles and cobbles with little clay under both phreatic and confined conditions (CGWB, 2007). These are relatively loose river borne valley filled deposits underlying the flood plains and the terraces of the river system. The average annual rainfall of the valley is about 1129.3 mm/year with approximately 64 rainy days in a year. Rainy season (July to September) gives around 83% of the rainfall forming the main source of groundwater recharge. The depth to groundwater level varies from near ground surface to 10 m below ground level (mbgl) (May 2014) in the main valley and increases towards the hills as the land surface rises (Fig. 2). Groundwater is being developed in the area by medium to deep tubewells, dug wells and dug-cum-bored wells. Depths of open dug wells and dug-cum-bored wells range from 4 to 60 m. The yield of shallow aquifer is moderate with well discharges going up to 10 L per second (lps). Deeper semi-confined aquifers are being developed by tubewells ranging in depth from 65 to 120 m tapping about 25–35 m granular zones (CGWB, 2008). Exploitation of the groundwater resources due to indiscriminate industrial activities

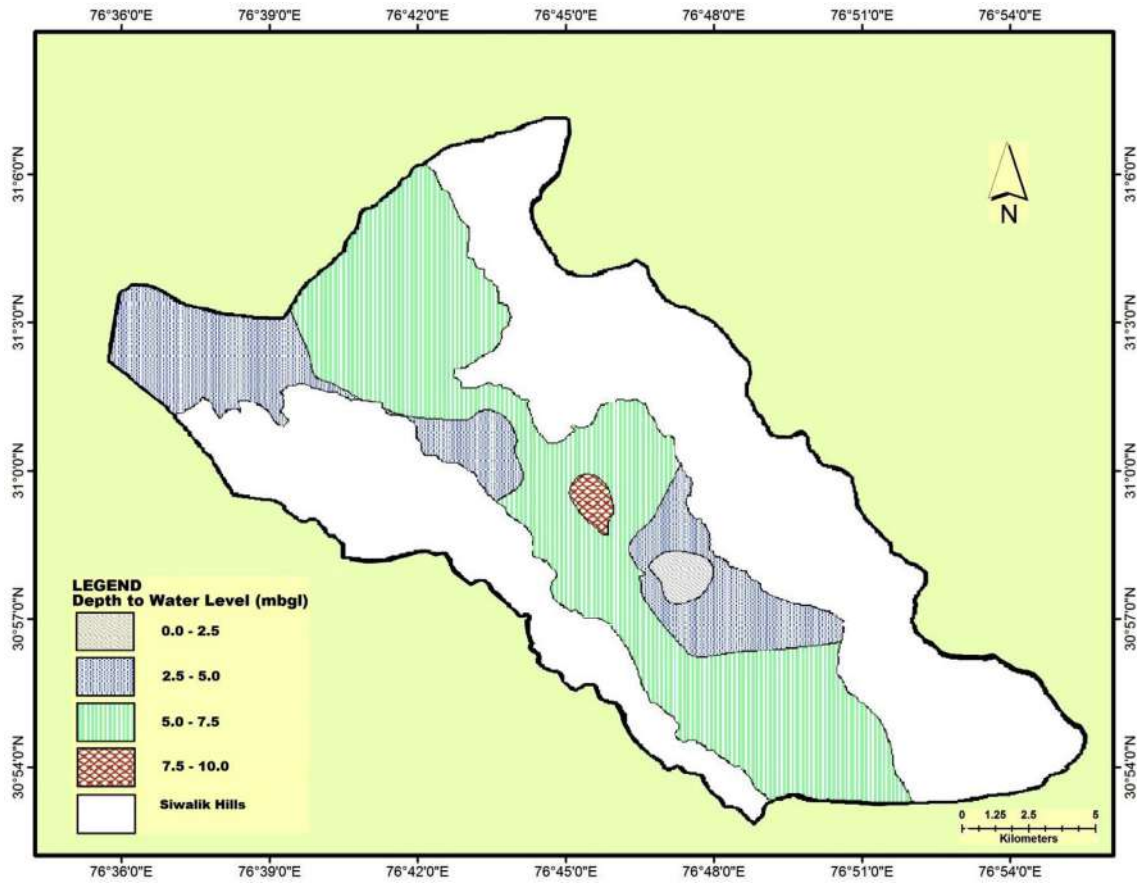


Fig. 2. Depth to water levels in the Nalagarh valley, Himachal Pradesh, India.

and rapidly growing unplanned urbanization has caused decline in the water levels (Herojeet et al., 2016). The area also lacks paved sewerage system and engineered sanitation facilities which cause leaching of the untreated domestic wastewater and industrial effluent into the subsurface.

3.2. Water chemistry and classification

Physicochemical and heavy metal composition of groundwater samples are presented in Table 3. Table 4 gives the descriptive

statistics that include minimum, maximum, mean, standard deviation and sample percentages exceeding the desirable and permissible limits prescribed by the Bureau of Indian Standards (BIS) (2012) and World Health Organization (WHO, 2017) for drinking water. Both pH and EC exceed these permissible limits in about 7% of the samples, whereas total dissolved solids (TDS) exceed the desirable limit in 53% of samples. Highest value of EC (1513 $\mu\text{S}/\text{cm}$) and TDS (922 mg/L) could be due to seepages from domestic wastewater and industrial effluents as the valley lacks adequate drainage facilities. Concentrations of the heavy metals

Table 3
Physicochemical and heavy metals composition of groundwater samples in Nalagarh valley, H.P., India.

S. No.	Locations	Longitude (degrees in decimal)	Latitude (degrees in decimal)	pH	EC $\mu\text{S}/\text{cm}$ at 25 °C	TDS mg/L											Σ Heavy Metal $\mu\text{g}/\text{L}$
							As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn		
G1	Lahrondi	76.8202	30.8947	7.86	569	370	6	4	0	19	150	93	65	37	119	0.493	
G2	Barotiwala	76.8394	30.9045	7.99	500	324	7	4	12	113	860	44	35	46	624	1.745	
G3	SitoMajra	76.8177	30.9095	8.7	535	347	4	4	6	17	18	13	56	41	248	0.407	
G4	Thar Majra	76.8353	30.9261	7.64	663	428	5	4	0	4	220	104	50	25	56	0.468	
G5	Dongrawala	76.8415	30.9216	8.21	688	446	9	0	21	9	298	10	12	16	78	0.453	
G6	Nariyanwala	76.8067	30.9181	7.27	844	548	2	7	4	4	490	31	85	30	563	1.216	
G7	Baddi	76.7965	30.9275	7.32	917	595	8	0	66	30	536	13	17	62	1180	1.912	
G8	Sandholi	76.7825	30.9384	7.29	1293	840	9	0	94	12	1366	59	32	23	213	1.808	
G9	Malpur	76.7798	30.9479	7.69	520	338	9	0	6	1	333	12	15	11	105	0.492	
G10	MakhruMajra	76.7822	30.9592	7.38	954	620	9	0	23	4	322	21	20	21	216	0.636	
G11	DalwalMajra	76.755	30.9731	7.46	760	492	7	0	73	13	1212	183	40	20	700	2.248	
G12	Manpura	76.7822	30.9873	7.17	1099	706	3	0	90	74	1021	192	52	18	811	2.261	
G13	KheraChak	76.7209	31.0102	7.44	846	547	10	0	23	27	395	19	11	20	63	0.568	
G14	DaddiKania	76.721	31.0411	7.30	1055	684	10	1	55	0	389	17	16	28	78	0.594	
G15	Nalagarh	76.7205	31.0973	7.30	1513	992	6	0	83	7	893	221	25	20	174	1.429	

Table 4
Statistical analyses of groundwater samples in Nalagarh valley, H-P, India.

Parameters	Units	Min.	Max.	Mean \pm Standard Deviation (SD)	Drinking Water					Primary Drinking Water Standard		
					WHO (2017)		BIS (2012)		USEPA (2019)			
					Guideline value (GV)	% above the GV	Desirable limits (DL)	Permissible limits (PL)	% above DL	% above PL	Maximum Contaminant Level (MCL)	% above MCL
pH		7.17	8.7	7.60 \pm 0.43	6.5–8.5	6.67	6.5–8.5		6.67			
EC	μ S/cm	500	1513	850.40 \pm 286.90	1500	6.67	1500 ^a		6.67			
TDS	mg/L	324	922	551.80 \pm 194.08	600	33.33	500	2000	53.33	Nil		
As	μ g/L	2	10	6.93 \pm 2.55	10	NIL	10	50	NIL	Nil	50	NIL
Cd	μ g/L	0	7	1.60 \pm 2.32	3	33.33	3		33.33		5	6.67
Cr	μ g/L	0	94	37.07 \pm 35.51	50	40.0	50		40.0		100	NIL
Cu	μ g/L	0	113	22.267 \pm 31.14	2000	NIL	500	1500	Nil	Nil	1300	NIL
Fe	μ g/L	8	1366	566.27 \pm 405.64	300	73.33	300		73.33			
Mn	μ g/L	10	221	68.80 \pm 73.54	100	26.67	100	300	26.67	Nil		
Ni	μ g/L	11	85	35.40 \pm 22.20	70	6.67	20		66.67			
Pb	μ g/L	11	62	27.87 \pm 13.47	10	100	10		100		15	86.67%
Zn	μ g/L	56	1180	348.53 \pm 343.57	3000	NIL	5000	15,000	Nil	Nil		

^a Since BIS (2012) does not specify any guideline value, WHO (2011) guideline value has been considered.

decrease as follows: Fe > Zn > Mn > Cr > Ni > Pb > Cu > As > Cd. While As, Cu, Mn and Zn concentrations are below the permissible limits for drinking water (BIS, 2012), As content is just touching the desirable limit of 10 μ g/L in 13% of samples and about 27% of samples shows Mn concentrations in excess of 100 μ g/L (desirable limit). The concentrations of Cd and Cr exceed the permissible limits (BIS, 2012) of 3 μ g/L and 50 μ g/L, respectively, in 33% and 40% of samples. Both Fe and Ni exceed their permissible limits in 73% (300 μ g/L) and 67% (20 μ g/L) of samples, respectively. Pb concentrations exceed the permissible limit (10 μ g/L) in all samples. The excess concentrations of Cd, Cr, Fe, Ni and Pb above the permissible limits and higher contents of Mn above the desirable limits in groundwater may be due to anthropogenic activities related to opencast mining of limestone and other construction materials, illegal disposal of industrial effluent and domestic sewerage besides geogenic inputs.

The method of Ficklin et al. (1992), modified by Caboi et al. (1999), has been applied for classification of groundwater. The relationship between the water pH and \sum heavy metals (As + Cd + Cr + Cu + Fe + Mn + Ni + Pb + Zn μ g/L) (Fig. 3) shows that 8 (53%) and 7 (~47%) sampling locations contain near neutral-low metals and near neutral-high metals, respectively. This method indicates the influence of heavy metals on pH at individual sampling locations.

3.3. Evaluation of pollution indices

Evaluation of groundwater contamination has been carried out by applying the conventionally used pollution indices (HPI, C_d , HEI) and the newly proposed HCI independently by using international standards (Edet and Offiong, 2002). Results are presented in Table 5. HPI values vary between 10.73 and 107.50 with a mean of 43.59. Except for G6 (107.50), all other sampling locations show HPI values less than the critical limit of 100 for drinking water (Prasad and Bose, 2001). The range and mean values of C_d are 1.31–37.87 and 17.06, respectively. The C_d values exceed 3 at 14 out of 15 sampling locations indicating high contamination level while one sampling location (G9) belongs to medium contamination level for domestic purposes (Backman et al., 1997). The HEI varies from 10.31 to 46.87 with a mean value of 26.06, but since there is no critical limit defined for HEI, assessment of contamination level in this method depends on the worker's discretion.

The critical limit of 100 in HPI method seems too broad a scale to assess water quality since the excess concentrations of a particular

trace metal can prove very harmful to human health and the environment. C_d computation does not take into account any analytical value that lies below the upper permissible limit for drinking water with the logic that such a concentration would not pose any health effect and environmental threat. Further, in C_d method, the analytical values need to be normalized, which increases the complexity of the evaluation process. In order to attain uniformity, since each chemical parameter contributes to the hydrochemical quality of a water body, it is essential that all analytical values are considered for evaluation process irrespective of whether these values lie above or below their respective permissible limits. HEI method does not have a scale for evaluation, and the interpretation is through multiple mean value approach (i.e., index values lying above or below the mean) to define the critical limit of a particular parameter. Therefore, the demarcation of a scale in HEI method becomes too arbitrary and study specific. From the above discussion, it really becomes very confusing as to which indexing method to use because of their limitations. An evaluative comparison of these pollution indices is shown in Suppl. Table S1, which is self-explanatory. HCI method, thus, has been developed to satisfy these limitations. HCI values in the study area range from 21.51 to 99.87 with a mean value of 60.17 (Table 5). All the groundwater samples are below the maximum of 100, although sampling locations G1, G2, G3, G4, G6, G8, G11, G12 and G15 show high HCI values. Further analyses are given below.

Linear regression is applied among the pollution indices and heavy metal parameter in order to identify the significant parameters influencing each pollution index. Table 6 presents the goodness of model (r value, significant at p value < 0.01 and < 0.05) between the pollution indices (HPI, C_d , HEI and HCI) and heavy metal parameters. While HPI shows strong correlation with four parameters As (r = 0.706), Cd (r = 0.963), Ni (r = 0.836) and Pb (r = 0.566), C_d and HEI have the similar loading on two parameters Pb (r = 0.915) and Zn (r = 0.703), respectively. The HCI, on the other hand, shows strong correlation with five parameters, namely As (r = 0.859), Fe (r = 0.546), Mn (r = 0.683), Ni (r = 0.756) and Pb (r = 0.859). The correlation between HPI, C_d , HEI and HCI is significant at p value < 0.01 and < 0.05. It becomes very clear from the regression analysis that among the pollution indices, the proposed HCI method has the maximum correlated parameters influencing the groundwater quality. A pollution index with more numbers of key contributing parameters reflects its authenticity and reliability as a method to provide valuable information on the overall status of heavy metal contamination in a water sample.

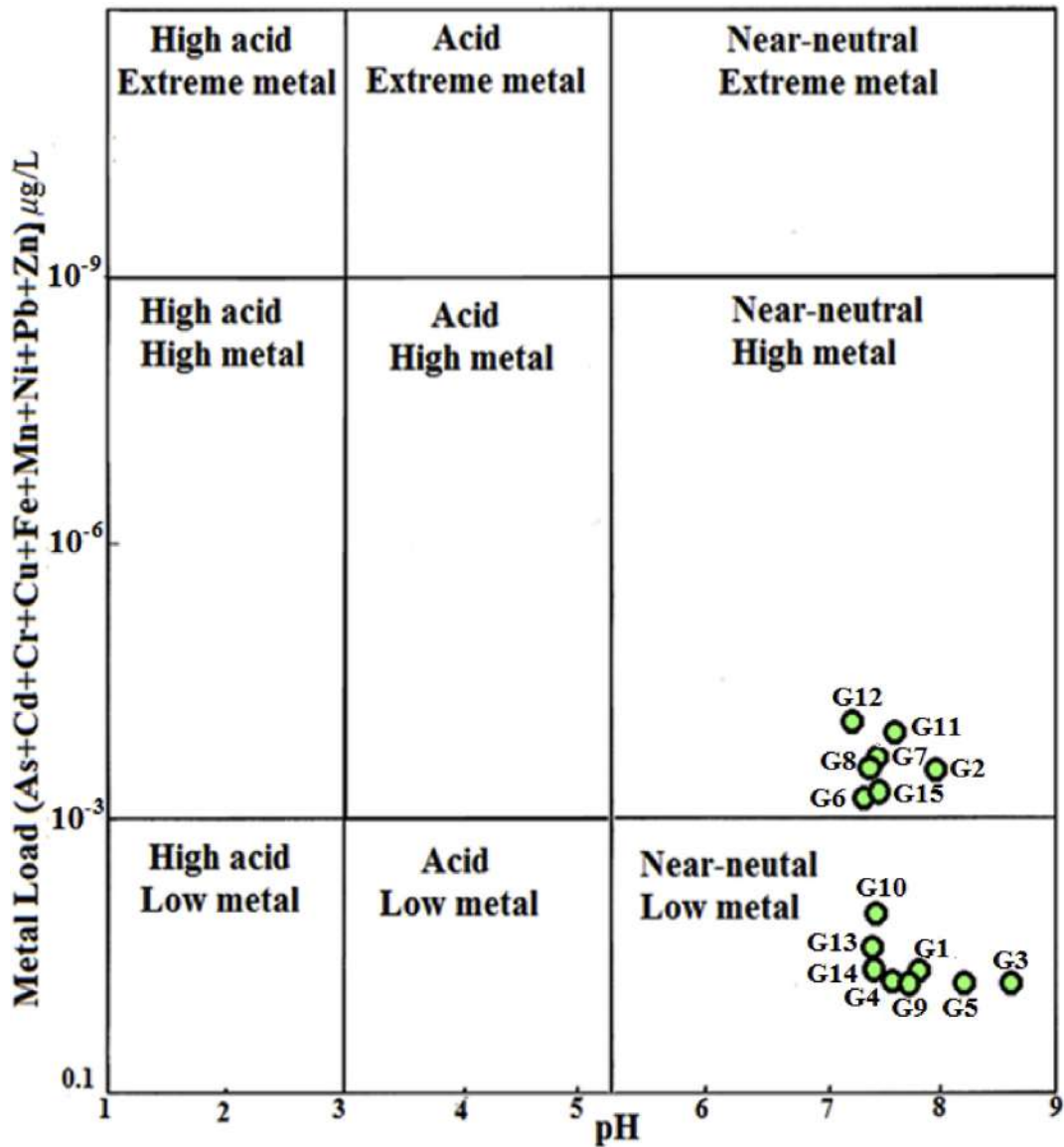


Fig. 3. Classification of groundwater samples (pH vs. metal load).

Table 5

Values of water pollution indices for individual sampling locations in the Nalagarh valley, H-P, India.

Sampling Locations	HPI	C _d	HEI	HCI
G1	78.753	23.023	32.023	74.6741
G2	76.777	30.548	39.548	65.095
G3	77.476	23.083	32.083	60.9569
G4	68.432	14.795	23.795	63.8741
G5	13.53	4.581	13.581	23.6268
G6	107.5	20.89	29.89	95.1433
G7	43.757	37.869	46.869	53.8607
G8	25.861	18.058	27.058	76.3437
G9	10.73	1.31	10.31	21.5113
G10	18.627	8.717	17.717	32.3771
G11	27.828	17.806	26.806	88.3789
G12	29.983	16.641	25.641	99.8721
G13	16.005	7.938	16.938	26.4596
G14	32.932	14.401	23.401	42.1225
G15	25.636	16.29	25.29	78.3302
Mean	43.588	17.063	26.063	60.1751
Min	10.73	1.31	10.31	21.5113
Max	107.5	37.869	46.869	99.8721

The mean deviation and the percent deviation with respect to the mean value of HCI (60.17) are enumerated for each sampling location in Table 7. The sampling locations (G1, G2, G3, G4, G6, G8, G11, G12 and G15) with high HCI values (Table 5) show high mean deviations and percent deviations (Table 7). The remaining sampling locations (G5, G7, G9, G10, G13 and G14) have lower HCI values than the mean value, and therefore show negative mean deviations and percent deviations. This simply indicates that the groundwaters quality at these locations are least influenced by heavy metals.

HCI values are further evaluated as per the newly developed water classes as shown in Suppl. Table S5. The sampling locations G5, G9, G10 and G13 fall in good water class (HCI values 21–40), G7 and G14 in marginal class (HCI values 41–60), G1, G2, G3, G4, G8 and G15 in poor class (HCI values 61–80) and G6, G11 and G12 in very poor class (HCI values 81–100), respectively. None of the sampling locations fall in excellent water class (HCI values 0–20). Similarly, no water sample falls under unfit category (HCI value > 100). As already discussed earlier, Pb (prescribed limit 10 µg/L) has been the violator parameter in all groundwater

Table 6
Correlation analysis between pollution indices and heavy metal parameters.

Parameters	HPI	C _d	HEI	HCI
As	0.706*	0.358	0.358	0.764
p value	0.003	0.019	0.190	0.001
Cd	0.963*	0.377	0.377	0.380
p value	0.000	0.166	0.166	0.163
Cr	0.486	0.153	0.153	0.388
p value	0.066	0.585	0.585	0.153
Cu	0.202	0.468	0.468	0.268
p value	0.470	0.078	0.078	0.335
Fe	0.262	0.184	0.184	0.546**
p value	0.345	0.511	0.511	0.035
Mn	0.087	0.063	0.063	0.683*
p value	0.758	0.825	0.825	0.005
Ni	0.836*	0.367	0.367	0.756*
p value	0.000	0.179	0.179	0.001
Pb	0.566**	0.915*	0.915*	0.859*
p value	0.028	0.000	0.000	0.000
Zn	0.194	0.703*	0.703*	0.405
p value	0.488	0.003	0.003	0.074
HPI	1	0.602**	0.602**	0.509**
p value		0.018	0.018	0.053
C _d	0.602**	1	0.99*	0.523**
p value	0.018		0.00	0.047
HEI	0.602**	0.99*	1	0.523**
p value	0.018	0.000		0.047
HCI	0.509**	0.523**	0.523**	1
p value	0.053	0.047	0.047	

Bold indicates strong correlation between the pollution indices and heavy metal parameters. Bold-Italics indicates goodness of model significant at p value <0.01 and <0.05. **Correlation is significant at the 0.05 level.

*Correlation is significant at the 0.01 level.

Table 7
Mean deviation and % deviation with respect to the mean value of HCI (61.92) for each sampling location.

S. Nos.	HCI mean deviations	HCI % deviations
G1	14.499	24.095
G2	4.920	8.176
G3	0.782	1.299
G4	3.699	6.147
G5	-36.548	-60.737
G6	34.968	58.111
G7	-6.314	-10.493
G8	16.169	26.869
G9	-38.664	-64.252
G10	-27.798	-46.195
G11	28.204	46.870
G12	39.697	65.969
G13	-33.716	-56.029
G14	-18.053	-30.000
G15	18.155	30.170

samples collected because of industrial nature of the study area. However, its concentration increases from superior to inferior water classes. For example, in 'good' water class, its concentrations vary between 11 and 21 $\mu\text{g/L}$ (Table 3), while in 'marginal' water class they range from 28 to 62 $\mu\text{g/L}$. Although in 'poor' and 'very poor' water classes Pb concentrations are lesser in some samples (G12, G15), other violator parameters have comparatively much higher concentrations. For example, in water sample G12 (very poor water class), Pb concentrations are 18 $\mu\text{g/L}$, but Cr and Ni concentrations are 90 and 52 $\mu\text{g/L}$, respectively, much above their respective permissible limits, i.e., 50 and 20 $\mu\text{g/L}$.

It is important to note here that good water class has a single violator parameter (Pb) depicting low toxicity, marginal water class has two violator parameters (Cr and Pb) suggesting moderate toxicity and poor to very poor water classes have multiple violator

parameters (Cd, Cr, Ni and Pb) indicating strong to excessive toxicity levels on human health. In 'good' water class public action may or not be necessary for dilution of contamination for drinking purposes. If at all a public action is necessary, the action level will be minimal and localized. For example, the maximum contamination level (MCL) of Pb allowed in drinking water before a public action is required is 15 $\mu\text{g/L}$ (USEPA, 2019; Jurgens et al., 2019) and the maximum deviation from this MCL is 6 $\mu\text{g/L}$ for sample G10 (Pb = 21 $\mu\text{g/L}$) that may need only milder treatment as per Lead Copper Rule suggested by USEPA (1991, 2019). In 'marginal' water class, however, public action may possibly be necessary for reduction of pollution level, so is the case with other water classes if the groundwater is to be used for drinking purposes. Lower order classes may, however, be used for other usages such as for irrigation and livestock depending on their contamination level as recommended by the Food and Agriculture Organization (FAO, 1994). It can thus be inferred that the newly developed HCI water classes not only allow understanding of the groundwater quality in each sampling location, but also conform with the regulatory limits and help in extracting the violator parameters as well as in assessing the toxicity level of each individual class on human health.

It is interesting to note here that the sampling locations that have negative mean deviation and percent deviation values fall in good and marginal water classes and have low to moderate toxicity level with least number of violator parameters, which denote better water quality. The remaining samples that have positive mean deviations and percent deviations have multiple violator parameters and show high risk of toxicity (poor and very poor) indicating that the groundwater samples are contaminated by heavy metals. Groundwater at these locations thus require proper treatment before human consumption. The metal distribution in the Nalagarh valley based on HCI water class is shown in Fig. 4. It is observed that the southwestern portion of the Barotiwala industrial area and Baddi industrial complex in central part fall under poor to very poor water classes. The findings of the proposed HCI method and associated water classes (Suppl. Table S5) are coherent with the results of the mean deviations and percent deviations found at each sampling location (Table 7).

3.4. Identification of heavy metal sources

Chemometric techniques, namely PCA and CA, were used to identify the different pollution sources affecting the analysed parameters of groundwater samples. Varimax rotation method extracted four linear PCs (Singh et al., 2004, 2005), which explains 86.4% of the overall variance (Table 8). Principal components (PCs) with loading coefficient of >0.75 (labeled bold) are highly significant while those between 0.5 and 0.75 (italics, bold) are moderately significant for PCA interpretation. Principal Component 1 (PC1) explains 34.4% of the total variance with strong negative loading on pH, strong positive loading on Cr, and moderate positive score on Fe and Mn indicating mineralized water due to high TDS and EC, which are controlled by lithogenic factor. High loading of Cr may be attributed to the dissolution and oxidation of chromite (FeCr_2O_4) present in the host rock (Hem, 1991; Chen et al., 2007). The weathering and dissolution of local bedrock is the key sources of Fe and Mn. Negative score on pH strongly controls the solubility of Fe and Mn in groundwater depending on anions content and redox potential, especially at near neutral pH (ATSDR, 2000; Lorite-Herrera et al., 2008).

Principal Component 2 (PC2) accounts for 22.6% of the total variance with strong positive loading on As and negative score on Cd and Ni. This may be attributed to the anthropogenic factors such as industrial effluent, unplanned urbanization and agricultural runoff (Wu et al., 2008; Huang et al., 2014; Wagh et al., 2018). The

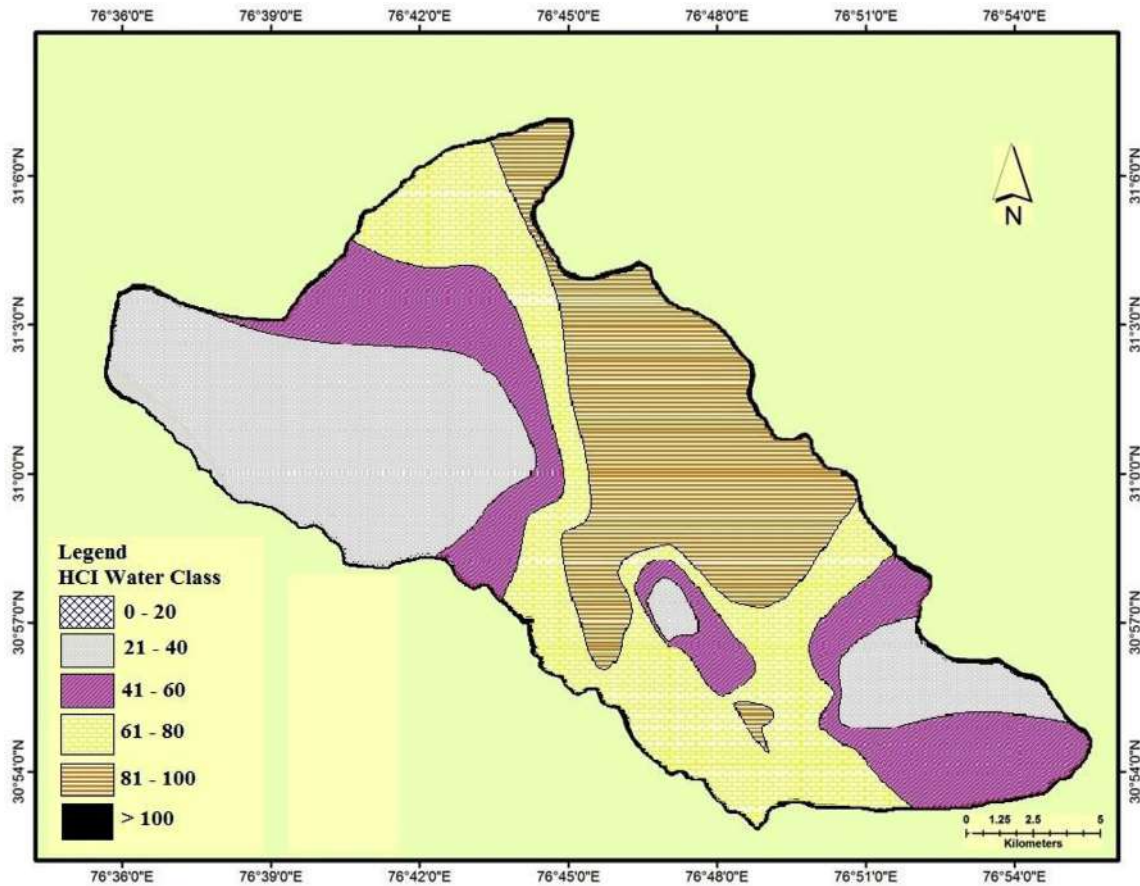


Fig. 4. Distribution of heavy metal pollution levels (based on HCl).

Table 8
Varimax rotated component matrix of the analysed groundwater samples.

Variables	PC1	PC2	PC3	PC4	Communality
pH	-0.815	-0.044	-0.003	0.032	0.667
EC	0.952	0.095	-0.067	0.100	0.929
TDS	0.950	0.095	-0.073	0.100	0.927
As	-0.013	0.941	-0.186	0.006	0.920
Cd	-0.408	-0.798	-0.171	-0.251	0.895
Cr	0.844	0.227	0.390	0.053	0.918
Cu	-0.190	-0.051	0.839	-0.218	0.791
Fe	0.628	0.057	0.626	0.160	0.815
Mn	0.506	-0.355	0.450	0.495	0.829
Ni	-0.086	-0.967	0.034	-0.039	0.945
Pb	-0.144	-0.153	0.176	-0.900	0.885
Zn	0.252	-0.165	0.635	-0.591	0.843
Eigen values	4.71	2.87	1.78	1.00	
% of variance	34.4	22.6	16.3	13.1	
Cumulative % of variance	34.4	57.0	73.3	86.4	
Probable sources	Lithogenic	Anthropogenic related to industrial effluent, unplanned urbanization and agricultural runoff	Weathering of bedrocks and oxidation of iron bearing minerals	Mixed factors (anthropogenic and geogenic processes)	

PC = Principal component. Bold indicates strong correlation between the pollution indices and heavy metal parameters. Bold-Italics indicates goodness of model significant at p value <0.01 and <0.05.

negative correlation of Cd and Ni with As indicates anthropogenic sources localized in the study area (Mehrabani et al., 2015). Arsenic contamination in the area comes mainly from paint, pharmaceutical, fertilizer and pesticide industries (Aradhi et al., 2009; Krishna and Mohan, 2014), while higher concentrations of Cd and Ni could be due to chemical, electrical, electronics and steel industries

(Table 1). Saadia et al. (2008) also suggest that Cd and Ni originate from industrial effluent and waste discharges from other types industries.

Principal Component 3 (PC3) is responsible for 16.3% of the cumulative variance that indicates strong positive score on Cu and gives moderate weight on Fe and Zn. Fe is uniformly distributed in

the earth's crust as the second most abundant element, while Zn and Cu too have about the same abundance in crustal rocks (Hem, 1991; Malle, 1992). While the concentrations of Cu and Zn are well within the desirable limits prescribed by the BIS (2012), Fe concentrations could be due to enhanced geogenic input resulting from opencast and limestone mining activities in the study area (Chirenje et al., 2007; Li et al., 2009; Herojeet et al., 2015; Hadzi et al., 2018).

Lastly, 13.0% variance is illustrated by Principal Component 4 (PC4) which puts positive weight on Mn (moderate) and negative score on Pb (strong) and Zn (moderate). The main sources of Zn are sphalerite, smithsonite and franklinite minerals found in the study area. The negative score on Zn is due to its adsorption on organic and inorganic sediments. With co-precipitation with manganese oxide, it tends to maintain low concentration levels in aquifers (Hem, 1976, 1980). Thus, the concentrations of Mn and Zn are well within the permissible limits of BIS (2012) reflecting natural factors. Both Pb and Zn exhibit similar geochemical behaviours in most natural processes (Reinmann and de Caritat, 1998; Mehrabi et al.,

2015). However, Pb concentrations are above the permissible limit in all samples (BIS, 2012). The enhanced levels of Pb could be due to agrochemical and industrial wastes released from fire equipment, paint and pigments, printing, plumbing and battery manufacturing plants (Romieu et al., 1994; Li et al., 2008; Devang et al., 2014) (Table 1). This component representing the Pb, Mn and Zn concentrations in groundwater is attributed to both anthropogenic activities and geogenic processes.

Cluster Analysis is used to create dendrogram by grouping 15 different sampling locations of groundwater. The difference between each cluster pattern can be explained by special parameters influencing them. Thus, the average value of each parameter within a cluster is calculated in order to identify the specific tracers for every cluster. Dendrogram divulges four clusters of significance $\{(D_{link}/D_{max}) * 100 < 30\}$ for groundwater (Fig. 5). Table 9 provides their average values. Cluster 1 (C1) includes parameters with the highest value of pH, Cd and Ni, and corresponds well with PC2. The sampling locations grouped in C1 (G1, G4, G3, G6) indicate that water pollution is primarily from the industrial effluent, sewage

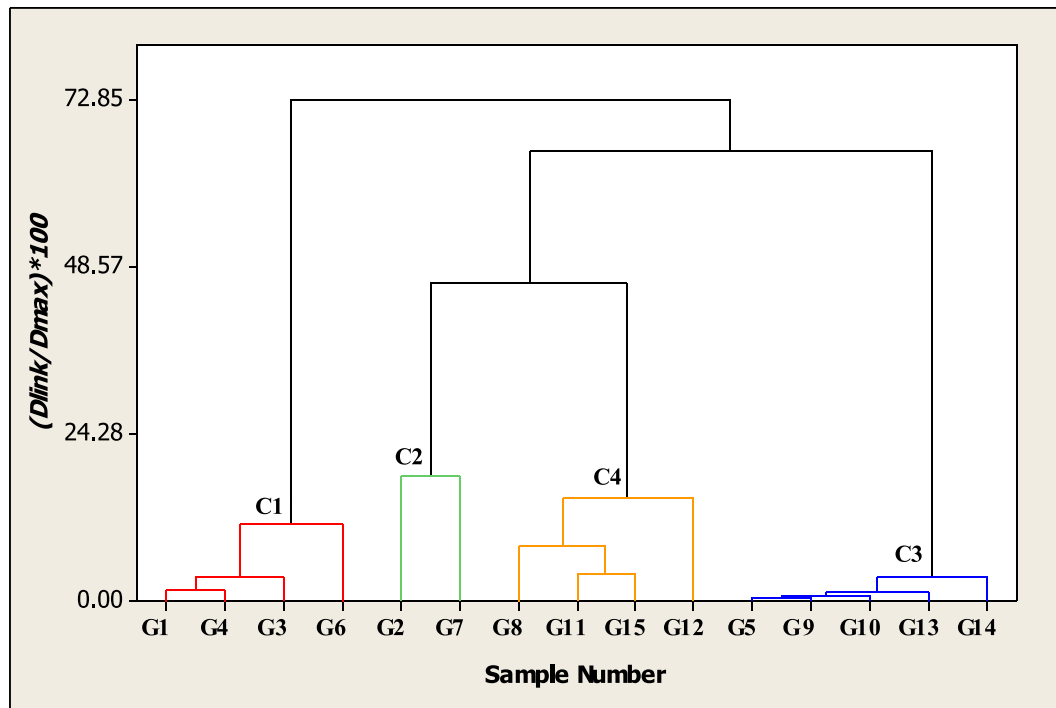


Fig. 5. Dendrogram of groundwater sampling locations.

Table 9

Average values of the heavy metal parameters for each cluster.

Parameters	C1 (G1,G4,G3,G6)	C2 (G2,G7)	C3 (G5,G9,G10,G13,G14)	C4 (G8,G11,G12,G15)
pH	7.87	7.66	7.60	7.31
EC ($\mu\text{S}/\text{cm}$)	652.75	708.5	812.6	1166.25
TDS (mg/l)	423.25	459.5	527	757.5
As ($\mu\text{g}/\text{L}$)	4.25	7.5	9.4	6.25
Cd ($\mu\text{g}/\text{L}$)	4.75	2.0	0.2	0
Cr ($\mu\text{g}/\text{L}$)	2.5	39.0	25.6	85
Cu ($\mu\text{g}/\text{L}$)	11.0	71.5	8.2	26.7
Fe ($\mu\text{g}/\text{L}$)	219.5	698.0	347.4	1123
Mn ($\mu\text{g}/\text{L}$)	60.25	28.5	15.8	163.75
Ni ($\mu\text{g}/\text{L}$)	64.0	26.0	14.8	37.25
Pb ($\mu\text{g}/\text{L}$)	33.25	54.0	19.2	20.25
Zn ($\mu\text{g}/\text{L}$)	246.5	902.0	108	474.5

Bold indicates the highest average value of a parameter among the four clusters. Bold-Italics indicates the second highest average value of a parameter to identify the special tracer.

and application of fertilizers and pesticides (OECD, 1994; WHO, 2005). Cluster 2 (C2) represents the smallest group of sampling locations (G2, G7), and is distinguished by the maximum values of Cu, Pb, Zn and higher loading of Fe, which may be attributed to the mixed factors (anthropogenic and geogenic). Geogenic contamination here could be due to mining activities (Amei and Akpah, 2011). Cluster 2 correlates well with PC3 and PC4. The largest set of sampling locations (G5, G9, G10, G13 and G14) belongs to cluster 3 (C3) that has only one parameter (As) corresponding to PC2. Cluster 3 may be due to As contamination and may be attributed to anthropogenic activities (Aradhi et al., 2009; Huang et al., 2014; Herojeet et al., 2015). Lastly, cluster 4 (C4) depicts a pattern with highest value of EC, TDS, Cr, Fe and Mn indicating that the naturally occurring geological host rocks (aquifers/aquitards) contribute to the water quality variations. The sampling locations (G8, G11, G12 and G15) in C4 embody background level (natural) of water quality as in PC1.

The integration of analyses by CA and PCA strongly authenticate that the groundwater is highly influenced by dissolution of local bedrocks, redox reactions in clay minerals and various anthropogenic inputs. Thus, the two statistical chemometric techniques (PCA and CA) show strong correlation in source apportionment as elucidated from data matrices of the groundwater samples.

Cluster Analysis has been used to validate findings of the proposed HCI method. When the sampling locations in each cluster are compared with HCI water classes, the possible factors influencing the contamination level in each water class are easily verified. Sampling locations belonging to C1 (Table 9) are contaminated due to anthropogenic factors and fall in poor to very poor HCI water classes (Suppl. Table S5). The sampling locations of C2 are controlled by mixed factors (geogenic and anthropogenic) and belong to marginal to poor water classes. The sampling locations in C3 are related to anthropogenic factors that have single special parameter (As), but HCI water class shows that the individual samples G5, G9, G10 and G13 that have relatively elevated As concentrations fall in good water class and G14 in marginal water class. This is due to fact that HCI calculates the overall heavy metal contents in water samples. In fact, As concentrations are 9 µg/L at three locations (G5, G9 and G10) and just touch the desirable limit of 10 µg/L at two locations (G13 and G14), but are well within the maximum permissible limit of 50 µg/L at all locations as per the BIS (2012) standards. Therefore, slightly elevated concentrations of As at these locations do not make much difference in classifying the groundwater as good water type. Finally, C4 sampling locations are controlled by the geogenic factors and fall in poor to very poor water classes. The concentrations of Cr and Fe (G8, G11, G12 and G15) and EC (G15) are above the permissible limits and TDS (G8, G12 and G15) and Mn (G11, G12, G15) above the desirable limits of BIS (2012) standards. The excess contents of these parameters render the sampling locations fall in poor to very poor HCI classes. All analyses show that the interpretations carried out by CA as well as HCI are supportive to each other in their findings. It can be inferred here that water quality decisions should not be made based on HCI alone; some chemometric technique, preferably CA (Lumb et al., 2011), should be used in combination with HCI water classes to have a better assessment of groundwater quality. Even if HCI classifies each sampling location into a different water class on the basis of the aggregate content of mixed trace elements and their toxicity level, CA identifies the potential heavy metals influencing them and their possible sources. Based on the HCI water classes and CA, remedial and preventive measures could be taken up at each sampling location to prevent further groundwater contamination. It becomes clear from the discussion above that the proposed HCI method has more advantages and diverse applicability to assess overall heavy metal contamination level in groundwater samples

compared to other indexing methods (HPI, C_d and HEI) discussed in this paper.

4. Conclusions

Various pollution indices (HPI, C_d and HEI) including the proposed indexing method, HCI, have been used along with the chemometric techniques to evaluate heavy metal contamination and identify the possible sources of groundwater contamination. Each conventionally used index has certain limitations in assessing groundwater pollution. The HPI sets a critical limit of 100 for drinking purposes, C_d exceeding 3 indicates heavy contamination for domestic uses, and HEI method does not specify any critical limit for human consumption. Application of these indices in Nalagarh valley, Himachal Pradesh, India shows that while almost all groundwater samples qualify for drinking purposes in HPI, above 90% of them are rejected for domestic uses in C_d and in HEI their assessment depends on the worker's discretion. It thus becomes very confusing as to which indexing method to use. The proposed HCI method satisfies this limitation by clearly assessing contamination level at each sampling location using mean deviation and percent deviation to classify the collected groundwater samples into different water classes. Regression analysis reveals that the HCI method has more significantly correlated key parameters than other indices justifying its greater reliability and wider applicability. Chemometric analyses by PCA and CA confirm that Cr, Cu, Fe, Mn and Zn are derived from lithogenic inputs and As, Cd, Ni and Pb from anthropogenic sources. Also, when the sampling locations of each cluster are compared with the HCI water classes, the violating parameters and their related sources become very clear. Therefore, the newly proposed HCI method has definite advantage over other indexing method in assessing heavy metal contamination.

Analyses reveal that the contamination level in Nalagarh valley, Himachal Pradesh, India gives a mixed picture in terms of groundwater pollution. Since significant parts of the area still have good quality groundwater, regulation is needed to monitor and protect the groundwater resources from pollution. This work, in particular, has significant implications for development of pollution reduction strategies in the foothill zones of the Indian sub-continent and elsewhere in the world to maintain a balance between the ecological integrity and industrialization, thereby minimizing the rate and extent of large-scale contamination in the future.

Author contributions

Herojeet Rajkumar: Conceptualization, Methodology, Investigation, Software, Formal Analysis, Data curation, Writing – original draft preparation, Pradeep K. Naik: Visualization, Supervision, Validation, Writing – Reviewing and Editing, Madhuri S. Rishi: Supervision, Resources

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125598>.

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