



Hydrogeochemical Evaluation of Groundwater of the steel city Durgapur, West Bengal, India

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Abstract

Quality assessment of groundwater of the steel city Durgapur, West Bengal, India, was carried out to investigate what roles anthropogenic activities and various hydrogeochemical processes play on it, employing combinations of hydrogeochemical analyses and two multivariate statistical techniques, namely, cluster analysis and principal component analysis. Values of analyzed parameters, namely, Na^+ , K^+ , Ca^{2+} , pH, electrical conductivity, total dissolved solids, hardness, Mg^{2+} , HCO_3^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and Cl reported wide variations which ranged from 49.50-248.50 mg/l, 1.70-225.00 mg/l, 29.70-217.40 mg/l, 4.90-6.83, 257-2501 $\mu\text{S}/\text{cm}$, 170-1273 mg/l, 16-568 mg/l, 1.90-48.60 mg/l, 40-520 mg/l, 0.99-15.42 mg/l, 0.02-1.00 mg/l, 6.51-182.46 mg/l and 19-314 mg/l respectively. Analyzed results demonstrated roles of natural hydrogeochemical processes like weathering of silicates and carbonates and exchange of ions as well as human-made developmental activities responsible for affecting the groundwater quality. Anthropogenic control on groundwater chemistry emerged as a basic concern especially in the industrial areas, where some assessed parameters recorded much elevated levels.

Keywords: Cluster analysis, geochemistry, piper diagram, principal component analysis.

Introduction

Twenty four regions in the country (India) can be designated as 'problem areas' where extensive industrial and other developmental activities dominate. In the state of West Bengal two such problem areas are Durgapur and Howrah. The Central Pollution Control Board (CPCB) examined groundwater quality of five selected locations in Durgapur industrial area and found physicochemical parameters exceeding the regulatory benchmark at some of the sites¹.

With this background information, a thorough investigation and geochemical characterization of groundwater quality of Durgapur, the emerging and future megacity of the Eastern India, by increasing the sample size is required to arrive at some discrete conclusions with respect to the occurrence of chemical components from natural sources, artificial means or from both. In addition to hydrogeochemical processes, developmental activities in the form of industrialization, urbanization, intensive agriculture and change in land use also control groundwater quality of a region and, therefore, their understanding is important for sustainable management, designing conservation plans and development of these freshwater resources. In India, several groundwater investigations have been taken up across the country; a few names include Gwalior city (Madhya Pradesh)², Muktsar district (Punjab)³, Deoria district (Uttar Pradesh)⁴, Akot city (Maharashtra)⁵ and Vaijapur, district Aurangabad (Maharashtra)⁶. This study is the first attempt to demonstrate and characterize groundwater chemistry of some selected industrial-commercial as well as residential zones of Durgapur employing combinations of hydrogeochemical

analyses and some advanced multivariate data analyses techniques.

Material and Methods

Study area: The study area, located between latitudes 23°35'09.42"N and 23°31'35.19"N; longitudes 87°11'48.54"E and 87°21'38.93"E, was a section of the Durgapur subdivision, Bardhaman district, West Bengal, India, figure-1. Many big and small industrial units are located here, notably, Durgapur Steel Plant, Durgapur Thermal Power Station, Alloy Steel Plant, Durgapur Cement and Durgapur Projects Limited. The industrial units and their townships have made Durgapur a flourishing urban-industrial region. Geologically the region is characterized by a thin occurrence of alluvial cover and presence of the Gondwana sedimentary rocks having continental sedimentary framework¹. Recent geo-environmental appraisal of the region distinguishes presence of four geomorphic units, namely, older alluvial surface, younger alluvial surface, present day surface and lateritic uplands⁷.

Sampling and analyses: Groundwater representative samples collected from twenty two strategically selected locations, figure-1, during March, 2013 were analyzed for the presence of major ions, namely, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} and HCO_3^- following standard procedures described by APHA⁸. Additionally, data of pH (measured at the sampling sites), electrical conductivity (EC), total dissolved solids (TDS) and hardness (HARD) were also obtained. Only double glass distilled and deionized waters and analytical grade reagents were used for the experiments.

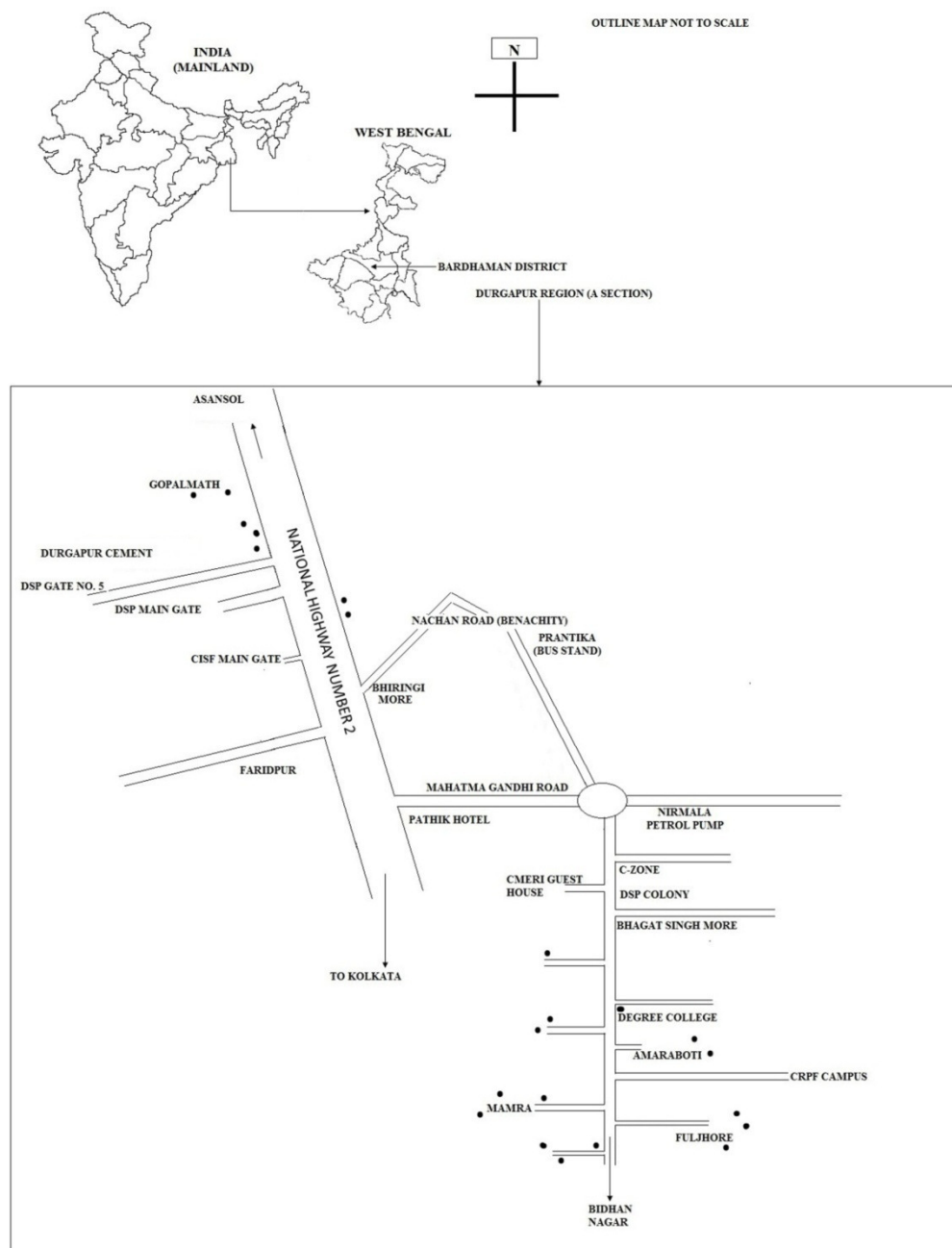


Figure-1
Study area (a section of the Durgapur subdivision) and sampling locations

Statistical analyses: Recorded physicochemical data were subjected to systematic statistical analyses, where, in addition to basic descriptive statistical tools and correlation analysis (Pearson), multivariate statistical techniques were applied on the dataset for intelligent interpretation of the hydrogeochemical data. Agglomerative hierarchical cluster analysis (AHCA) and principal component analysis (PCA) multivariate tools were employed in the present investigation. Dataset was checked for its normal distribution character following statistical protocols like *P-P* plots, *Q-Q* plots, mean-median comparison, skewness

and kurtosis. Accordingly, data were log transformed to approach normal distribution and also removing the influence of outliers. Water chemistry being a multivariate data comprising many variables, some sophisticated statistical methodologies is required for its comprehensive appraisal. Many hidden phenomena and inherent multifaceted hydrochemical behaviours can be expressed through multivariate modeling methods without much loss of original information. Multivariate data analyses systems provide concurrent examination of several variables both in space and time⁹.

AHCA is done for classifying an ungrouped data into homogeneous sets of related observations based on their similarities and the result is presented as a dendrogram. This study used Ward's method and squared Euclidean distance, as a measure of proximity, for the classification of sampling sites. The Euclidean distance is expressed as given below¹⁰.

$$d_{ij} = \left[\sum_{l=1}^q (x_{il} - x_{jl})^2 \right]^{1/2}$$

Where, d_{ij} = Euclidean distance for two individuals i and j (d_{ij}^2 = squared Euclidean distance), each measured on q variables, x_{il} , x_{jl} , $l = 1 \dots q$.

PCA is an intelligent dimension reduction technique which reduces a large dataset into a new set of linear combination of variables designated as principal components (PC). In other words, each orthogonal PC is a linear combination of the original variables and denotes a different variation source¹¹. These PCs disclose information about the most significant variables explaining the complete dataset by rendering exclusion of the variables considered less significant, while still retaining original information with minimum loss^{12,13}. The PCs generated through PCA can be expressed as¹⁴:

$$y_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + a_{i4}x_{4j} + \dots + a_{im}x_{mj}$$

Where y = component score, a = component loading, x = measured value of the variable, i = component number, j = sample number, and m = total number of variables. In the present study, Kaiser Normalization along with VARIMAX rotation was employed for the generation of PCs.

Results and Discussion

Groundwater physicochemical profile: Assessment of hydrochemical parameters is essential to evaluate groundwater quality and assign contaminated or uncontaminated nature. Moreover, generated data is employed in investigating various hydrogeochemical mechanisms responsible for controlling geochemistry of groundwater. Study of water quality is indispensable to understand aquatic ecosystem¹⁵. Analyzed parameters reported wide variation and range values, figure-2 and table-1, suggesting role of different factors in controlling chemistry of the aquifer systems. Parameters like Na^+ , K^+ , Ca^{2+} , Cl^- , Mg^{2+} , HCO_3^- , TDS and EC crossed the desirable regulatory standards of the World Health Organization¹⁶ and the Bureau of Indian Standards¹⁷ for drinking water at some of the sites, mostly industrial areas, indicating occurrence of influence of human-made developmental activities on the groundwater quality. As TDS is directly dependent on the concentration of ions, its distribution in groundwater of the area is demonstrated in figure-3. In Pearson's correlation analysis, table-2, most of the parameters displayed strong association indicating possible interactions between them. Significantly high correlation ($P < 0.05$) was noted for $\text{Na}^+ - \text{K}^+$, $\text{Na}^+ - \text{Ca}^{2+}$, $\text{Na}^+ - \text{SO}_4^{2-}$, $\text{Na}^+ - \text{Cl}^-$, $\text{K}^+ - \text{Cl}^-$, $\text{Ca}^{2+} - \text{HCO}_3^-$, $\text{Ca}^{2+} - \text{SO}_4^{2-}$, $\text{Ca}^{2+} - \text{Cl}^-$, $\text{Mg}^{2+} - \text{HCO}_3^-$, $\text{Mg}^{2+} - \text{SO}_4^{2-}$, $\text{HCO}_3^- - \text{SO}_4^{2-}$ and $\text{SO}_4^{2-} - \text{Cl}^-$. Parameters demonstrating high correlation may suggest similar origin and associated controlling processes. EC exhibited strong correlation ($P < 0.05$) with Na^+ (0.92), Ca^{2+} (0.99), SO_4^{2-} (0.94), Cl^- (0.75) and relatively good relation with K^+ (0.52) and HCO_3^- (0.62) implying involvement of most of the ions in controlling groundwater physicochemical processes such as oxidation-reduction and exchange of ions⁴. Highest correlation of Na^+ was observed with Cl^- (0.89, $P < 0.05$) suggesting contribution of artificial (anthropogenic) sources to the groundwater chemistry⁴.

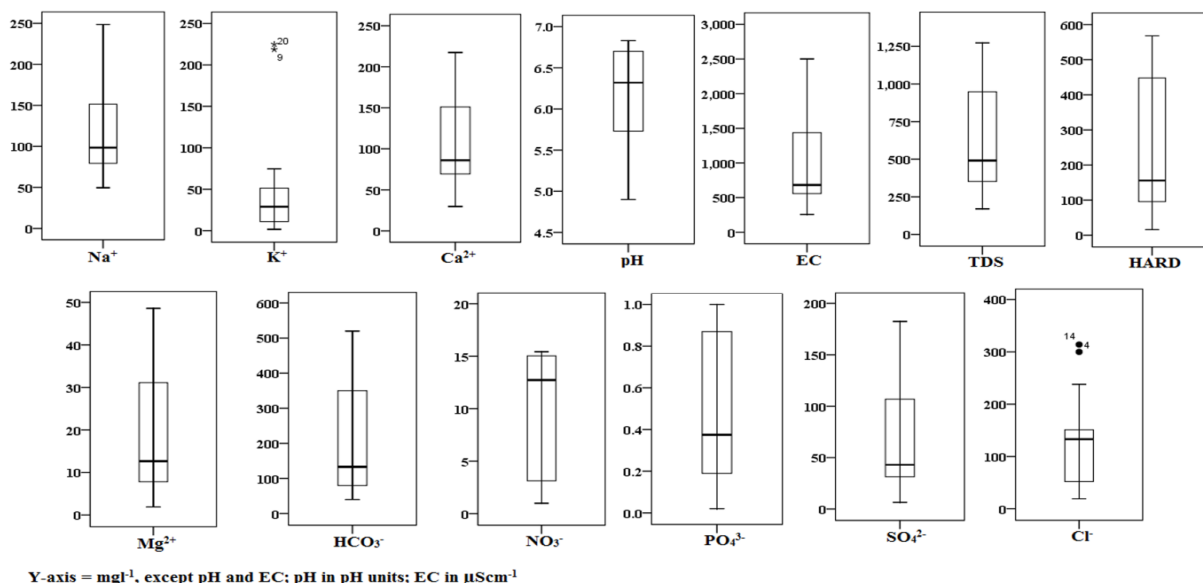


Figure-2
 Box and whisker plots showing distribution of analyzed physicochemical parameters in groundwater samples

Table-1
Descriptive geo-statistics of the analyzed groundwater samples and some guideline values

AP	Min	Max	Mean	SD	Med	Skewness	Kurtosis	BIS (2004) Desirable limit*	#WHO (1997) Desirable limit
Na ⁺	49.5	248.5	122.7	60.94	98.5	1.2	0.185	-	50
K ⁺	1.7	225	46.9	60.95	28.95	2.35	5.25	-	100
Ca ²⁺	29.7	217.4	103.9	50.95	86.05	0.982	0.262	75	75
pH	4.9	6.83	6.2	0.59	6.32	-0.67	-0.461	6.5-8.5	7.0-8.5
EC	257	2501	998.8	635.06	682	1.29	0.95	-	750
TDS	170	1273	619.1	323.01	491	0.72	-0.61	500	500
HARD	16	568	255.4	187.74	156	0.46	-1.459	300	100
Mg ²⁺	1.9	48.6	18.3	14.78	12.65	0.969	-0.338	30	30
HCO ₃ ⁻	40	520	205.9	161.68	133	0.775	-0.992	200*	200
NO ₃ ⁻	0.99	15.42	9.8	5.72	12.73	-0.33	-1.78	45	-
PO ₄ ³⁻	0.02	1.0	0.47	0.33	0.38	0.36	-1.44	-	-
SO ₄ ²⁻	6.51	182.5	71.4	58.09	42.99	0.9	-0.51	200	200
Cl ⁻	19	314	122.1	87.01	133	0.855	-0.012	250	250

Cations, anions, TDS and HARD in mg/l; EC in μ S/cm; * and # adopted from other source²³; AP = analyzed parameters, min = minimum, max = maximum, SD = standard deviation, med = median

Table-2
Correlation analysis of the groundwater quality dataset

	Na ⁺	K ⁺	Ca ²⁺	pH	EC	TDS	HARD	Mg ²⁺	HCO ₃ ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻
Na ⁺	1.0	0.66	0.88	0.31	0.92	0.89	0.68	0.25	0.34	0.45	0.15	0.77	0.89
K ⁺		1.0	0.43	-0.26	0.52	0.56	0.18	-0.05	-0.28	0.73	0.14	0.45	0.81
Ca ²⁺			1.0	0.65	0.99	0.98	0.92	0.49	0.69	0.04	0.43	0.95	0.69
pH				1.0	0.58	0.56	0.79	0.65	0.92	-0.57	0.49	0.69	0.09
EC					1.0	0.99	0.86	0.40	0.62	0.14	0.35	0.94	0.75
TDS						1.0	0.85	0.43	0.61	0.12	0.43	0.96	0.77
TH							1.0	0.76	0.79	-0.27	0.49	0.90	0.42
Mg ²⁺								1.0	0.52	-0.44	0.45	0.54	0.06
HCO ₃ ⁻									1.0	-0.62	0.42	0.72	0.07
NO ₃ ⁻										1.0	-0.29	-0.07	0.68
PO ₄ ³⁻											1.0	0.45	0.21
SO ₄ ²⁻												1.0	0.61
Cl ⁻													1.0

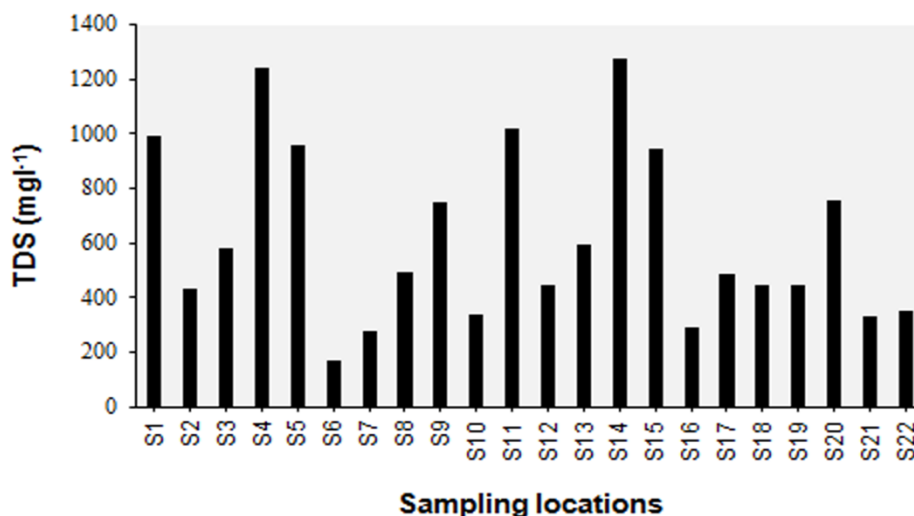


Figure-3
 Spatial distribution of analyzed TDS in groundwater samples

Hydrogeochemical evaluation: Piper trilinear plot, developed for investigating evolution of hydrogeochemical parameters, classified collected groundwater samples into four distinct types, namely, $\text{Ca}^{2+}\text{—HCO}_3^-$, Mixed $\text{Ca}^{2+}\text{—Mg}^{2+}\text{—Cl}^-$, Mixed $\text{Ca}^{2+}\text{—Na}^+\text{—HCO}_3^-$ and $\text{Na}^+\text{—Cl}^-$. Accordingly, 40.91%, 18.18%, 27.27% and 13.64% samples belonged to four identified water types respectively. The evaluation further revealed 68.18% water samples represented temporary hardness of water. Since, the study area lies adjacent to the Damodar river basin rich in coal deposits, this classification was also supported by the work of Jayaprakash *et al.*¹⁸ who reported hydrochemical facies of Mixed $\text{Ca}^{2+}\text{—Na}^+\text{—HCO}_3^-$, Mixed $\text{Ca}^{2+}\text{—Mg}^{2+}\text{—Cl}^-$, $\text{Na}^+\text{—Cl}^-$ and $\text{Ca}^{2+}\text{—HCO}_3^-$ types from the Neyveli groundwater basin (India). Piper plot illustrating water types are displayed in figure-4.

Identifying hydrogeochemical processes controlling groundwater chemistry is essential to discover key sources affecting its quality. The ion exchange chemistry between subsurface waters and the surrounding environment is a major phenomenon that controls distribution and occurrence of ions in the former¹⁹. This hydrogeochemical process can be evaluated employing chloro-alkaline indices (CAI-1 and CAI-2) suggested by Schoeller²⁰ and also described in literature of other authors^{3, 21, 22}. The CAIs can be computed from the formulae given below (ions expressed in meq/l).

$$\text{CAI} - 1 = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]/\text{Cl}^-$$

$$\text{CAI} - 2 = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]/[\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-]$$

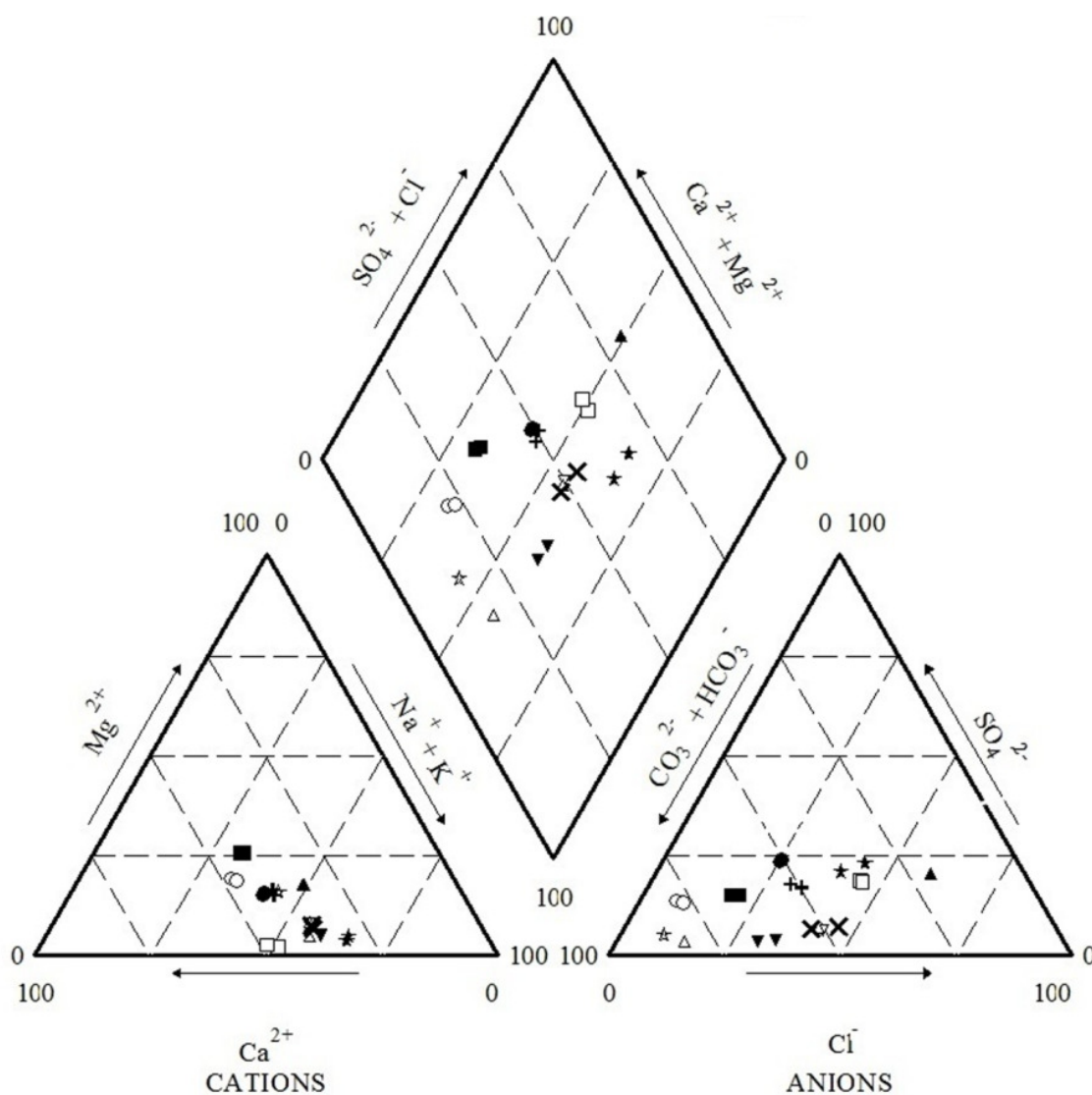


Figure-4
 Piper trilinear plot illustrating hydrochemical regime of the groundwater samples

When Na^+ and K^+ ions present in the groundwater are exchanged with Ca^{2+} and Mg^{2+} present in the surrounding rock, the CAIs are positive and the exchange is known as direct. This reaction is also called base-exchange reaction and the resulting condition chloro-alkaline equilibrium. Whereas, in reverse process the CAIs are negative and the exchange is known as indirect. This reaction is also called cation-anion exchange reaction and the resulting condition chloro-alkaline disequilibrium^{21,23}. CAIs calculated for the groundwater samples showed negative values (result not shown) which illustrated prevalence and existence of cation-anion exchange process and chloro-alkaline disequilibrium respectively. Another method to determine underlying mechanism controlling groundwater quality is the Gibbs plot. In TDS versus $[\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})]$ plot most of the chemical data, except a few, plotted in the rock weathering dominance zone, figure-5. Similar plot was noted for TDS versus $[\text{Cl}/(\text{Cl} + \text{HCO}_3^-)]$, figure-6, indicating control of rock-water interaction in hydrogeochemistry of the region. Two plots, namely, Na^+ versus Cl^- and Na^+/Cl^- versus EC also demonstrate whether evaporation is a major controlling factor of the groundwater chemistry. If evaporation is the dominant process for increasing concentration of chemical species then the ratio of Na^+/Cl^- would remain unchanged presuming that no mineral species have undergone precipitation, and consequently Na^+/Cl^- versus EC would produce a horizontal plot^{3,24}. A molar ratio of Na^+/Cl^- approximating one indicates halite dissolution whereas ratio greater than one points to weathering of

silicates^{3,25}. The recorded molar Na^+/Cl^- ratios typically disclosed silicate weathering as one of the factors, except at two stations where halite dissolution was noted, figure-7. The plot of Na^+/Cl^- versus EC, figure-8, illustrated slightly inclined trend suggesting weathering and exchange of ions, and not evaporation, were the prevalent hydrogeochemical processes which affected groundwater chemistry of the area. In the plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus $(\text{SO}_4^{2-} + \text{HCO}_3^-)$ chemical data points featuring along the equiline indicate presence of ions in groundwater from weathering of both carbonates and silicates while points falling above or below the equiline suggest carbonate weathering or silicate weathering as dominant process respectively. Data points in figure-9 clearly indicated coupled weathering involving both carbonates and silicates. Existence of coupled weathering was also demonstrated by $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus HCO_3^- , figure-10; $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus total cations, figure-11; and $(\text{Na}^+ + \text{K}^+)$ versus total cations, figure-12, plots. The ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ is used for source identification of Ca^{2+} and Mg^{2+} as the mole ratio around one indicates weathering of minerals. The graphical representation, figure-13, evidently pointed that weathering was not the only source of alkaline earths in groundwater. In addition to reverse ion exchange, anthropogenic contribution could also be attributed²⁶. With the increase of $(\text{SO}_4^{2-} + \text{Cl}^-)$ the alkalis also reported increasing trend, figure-14, which suggested a common source for these ions and the occurrence of Na_2SO_4 and K_2SO_4 in soils⁴ of the Durgapur area.

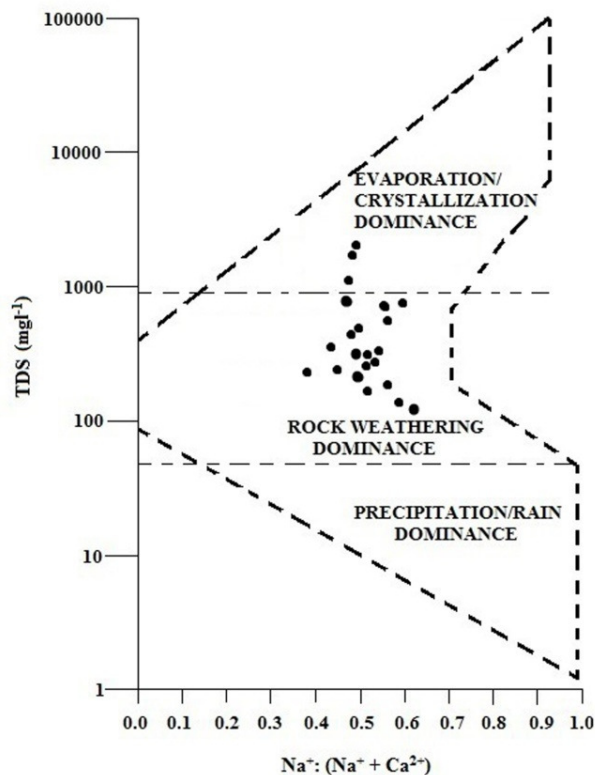


Figure-5
 Gibbs plot showing TDS versus $\text{Na}^+ : (\text{Na}^+ + \text{Ca}^{2+})$ hydrogeochemistry

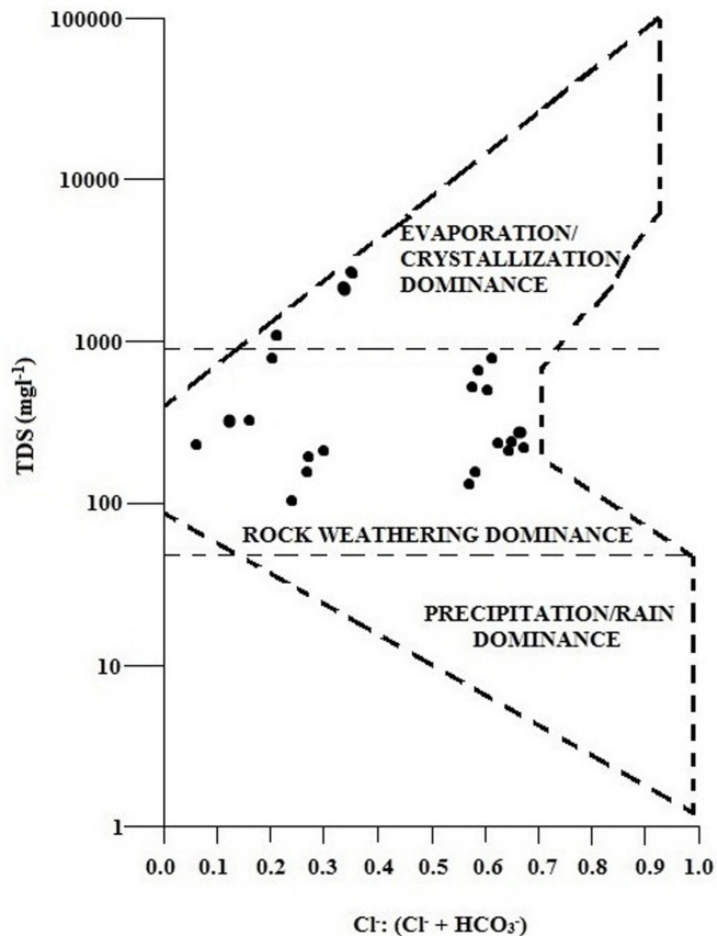


Figure-6
Gibbs plot showing TDS versus Cl:(Cl + HCO₃) hydrogeochemistry

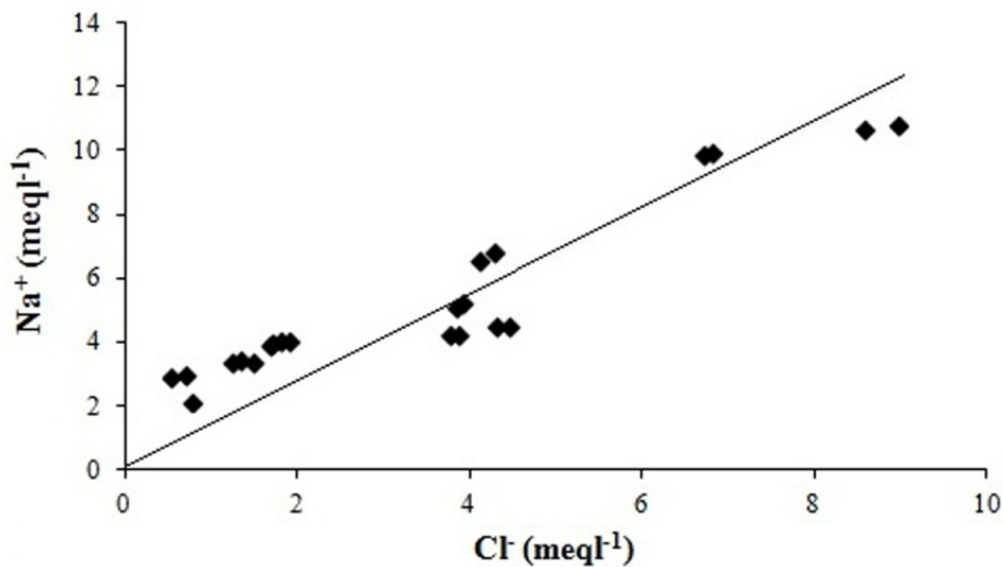


Figure-7
Scatter plot of Na⁺ versus Cl⁻ obtained from the hydrogeochemical data

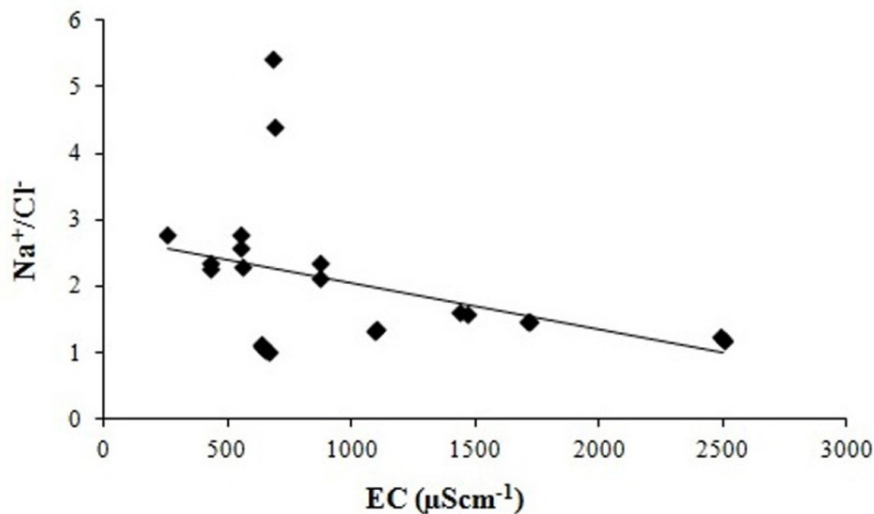


Figure-8

Scatter plot of Na^+/Cl^- versus EC obtained from the hydrogeochemical data

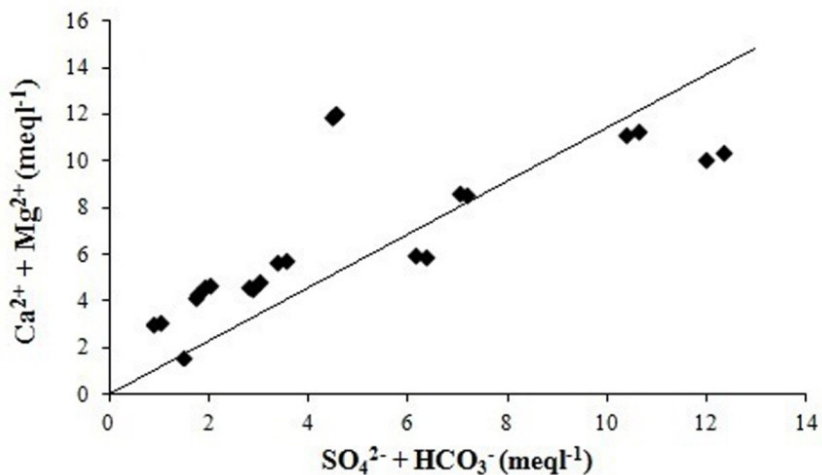


Figure-9

Scatter plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus $(\text{SO}_4^{2-} + \text{HCO}_3^-)$ obtained from the analyzed groundwater samples

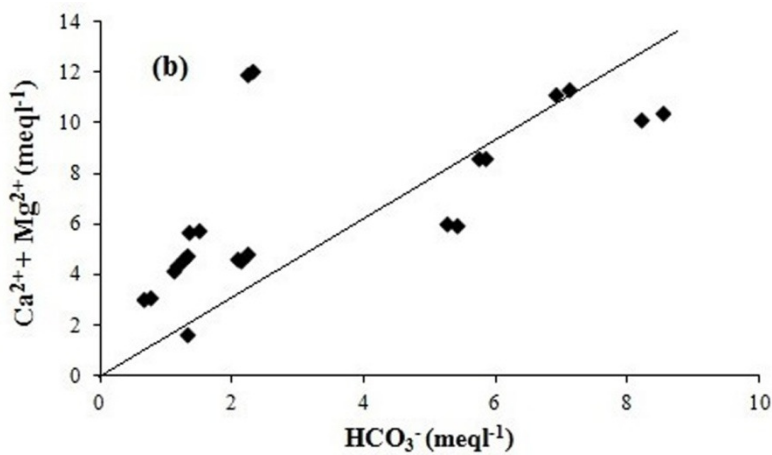


Figure-10

Scatter plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus HCO_3^- obtained from the analyzed groundwater samples

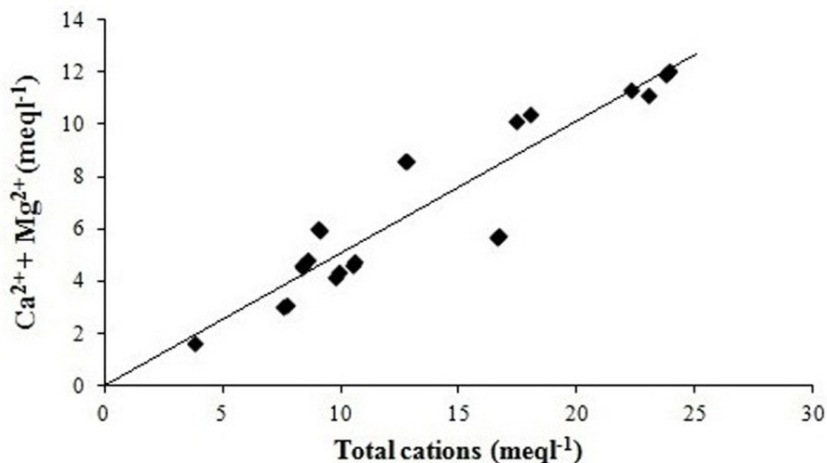


Figure-11

Scatter plot of (Ca²⁺ + Mg²⁺) versus total cations obtained from the analyzed groundwater samples

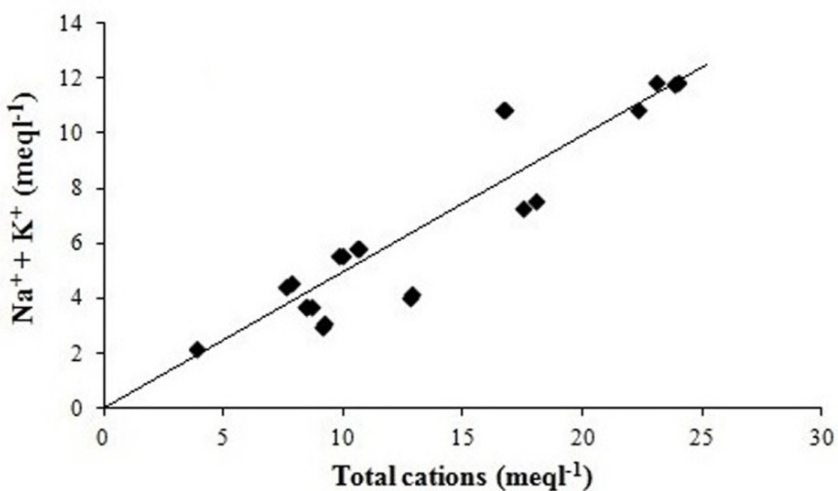


Figure-12

Scatter plot of (Na⁺ + K⁺) versus total cations obtained from the analyzed groundwater samples

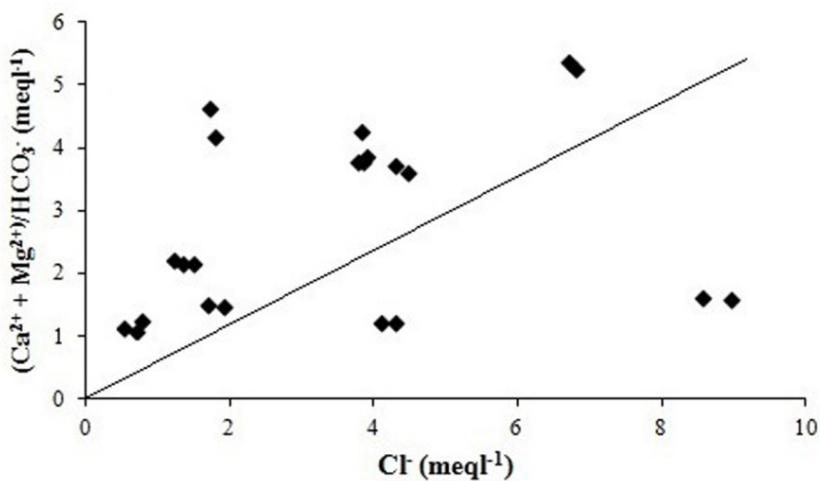


Figure-13

Scatter plot of (Ca²⁺ + Mg²⁺)/HCO₃⁻ versus Cl⁻ obtained from the analyzed groundwater samples

Multivariate statistical analyses: AHCA performed on standardized dataset, to organize groundwater sampling sites into groups based on their spatial resemblance, generated four statistically significant clusters, figure-15. Accordingly, the resultant model effectively classified four groups based on developmental activities as industrial zone (group 1), organized residential zone (group 2), organized residential-cum-market zone (group 3) and unorganized residential zone (group 4) suggesting control of human-actions on groundwater quality.

This investigation successfully established AHCA as a potent exploratory data analysis model which can be employed extensively for spatial classification and categorization of water resources and their management. As environmental management of freshwater resources requires constant monitoring and assessment, cluster analysis effectively reduces number of sampling sites recognizing some representative samples which could be suggestive enough to predict water quality of the whole area.

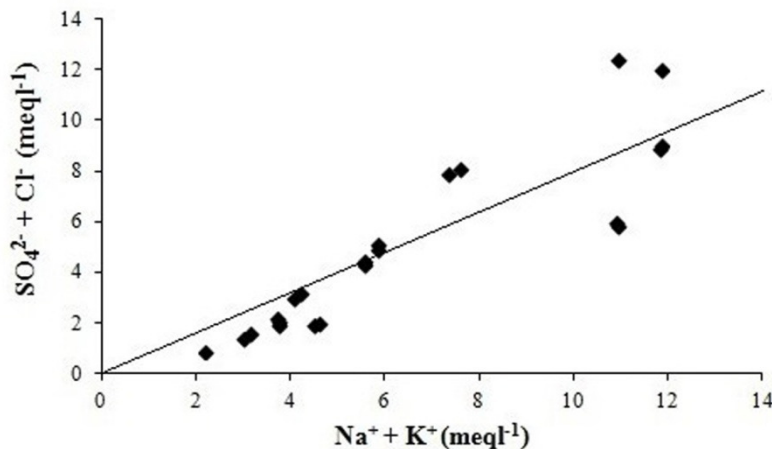


Figure-14

Scatter plot of (SO₄²⁻ + Cl⁻) versus (Na⁺ + K⁺) obtained from the analyzed groundwater samples

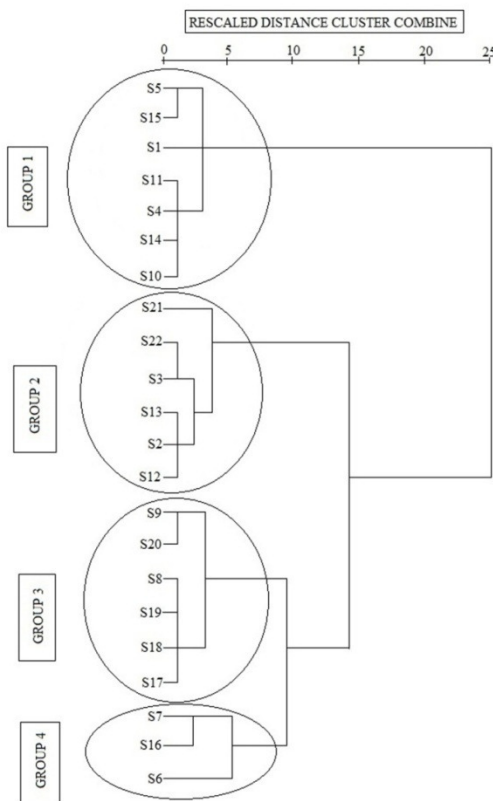


Figure-15

AHCA as dendrogram displaying four spatially homogeneous groups of the groundwater sampling sites

PCA with VARIMAX rotation generated three principal components (PCs) together accounting for 90.63% of the variance in the hydrogeochemical dataset, table-3. PC1 loaded with Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} , accounted 41.34% variance and represented silicate weathering. PC2, dominated with factor loadings of Na^+ , K^+ and Cl^- , accounted 40.20% of the variance and specified events of carbonate weathering along with cation-anion exchange reactions. Thus, PCA established occurrence of mixed weathering in aquifer systems of the area (also suggested by re-emergence of PC1 dominant ions in PC2). Exhibition of almost similar variance by PC1 and PC2 demonstrated that the groundwater chemistry of the area was overwhelmingly controlled by the behaviour of ions. However, Na^+ , Cl^- and HCO_3^- along with Ca^{2+} were predominantly involved in controlling the ionic properties. Water classification evaluated through modeling Piper plot also confirmed this noted observation. Presence of TDS and its surrogate partner EC with relatively close and high factor loadings in both PC1 and PC2 suggested that in addition to underlying geology, some artificial factors also influenced groundwater chemistry of the Durgapur area. For examples, domestic water use causes elevation of the TDS concentration with the addition of salts, detergents and other household by-products; dissolution of minerals in the subsurface and a corresponding increase in the TDS level of the water can also occur from aerobic oxidation of domestic-waste effluent (which causes acidity)²⁷. Contaminated artificial recharge water from large industrial complexes, such as downward migration of liquids discharged (from spills and inadequate control of wastes) onto the ground surface and leaching of unsheltered stockpiles of solid materials can also increase TDS concentration of the groundwater. Residential developments can also influence the water quality that recharges aquifers²⁸. PC3 accounted 9.09% of the variance and displayed dominance of PO_4^{3-} . As NO_3^- showed high loading in PC2 independent of PC3, and, since, PO_4^{3-} and NO_3^- represent both inorganic and organic pollution load, mixing of polluted water with the sub-surface water from various sources, industrial, agricultural (application of chemical fertilizers) and domestic wastes (for example, domestic sewage), was likely to happen. PC3 having high loading of PO_4^{3-} suggested its predominant presence in water from industrial and domestic outcomes.

Conclusion

The present investigation markedly demonstrated hydrogeochemical processes like weathering of rocks and exchange of ions between aquifer materials and the sub-surface water as well as human-made developmental activities influenced groundwater quality of the steel city Durgapur. Anthropogenic influence on groundwater chemistry, which emerged as a basic concern in this research work needs more detailed study by further increasing the sample size, including seasonal studies, and chemical parameters. The baseline information reported in this study is the first step in this direction. Moreover, studies on occurrence of trace elements in groundwater of the Durgapur subdivision should immediately

be taken up. This communication also illustrated that hydrogeochemical analyses and multivariate statistical techniques together provide valuable insights into comprehensive characterization of the groundwater quality.

Table-3
Rotated component matrix of PCA of the groundwater quality dataset

	Rotated Component		
	1	2	3
Na^+	0.360	0.900	-0.039
K^+	-0.232	0.897	0.159
Ca^{2+}	0.715	0.677	0.099
pH	0.906	-0.015	0.059
EC	0.641	0.755	0.010
TDS	0.626	0.759	0.102
HARD	0.817	0.420	0.281
Mg^{2+}	0.692	0.000	0.376
HCO_3^{2-}	0.962	-0.015	-0.032
NO_3^-	-0.620	0.731	-0.128
PO_4^{3-}	0.155	0.064	0.942
SO_4^{2-}	0.755	0.604	0.066
Cl^-	0.074	0.962	0.045
Eigenvalue	5.375	5.226	1.182
% of variance	41.34	40.20	9.09
Cumulative %	41.34	81.54	90.63

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