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Assessment of groundwater quality, toxicity and health risk in an industrial area using multivariate statistical methods

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Abstract

Background: This study investigates the common and anthropogenic activities that impact the science of groundwater in and around an industrial zone and exhibits the utilization of multivariate statistical methods for groundwater quality, toxicity and health risk associated with contaminated industrial sites for proficient administration of water assets. A total of 120 groundwater samples were collected during summer and winter season, and analyzed for their twenty physicochemical constituents including seven toxic heavy metals (pH, EC, total dissolved solids (TDS), F, K, Na, Ca, Mg, Cl, CO_3, HCO_3, NO_3, SO_4, As, Cd, Cr, Cu, Ni, Pb and Zn). Data obtained was treated using principal component analysis (PCA)/factor analysis (FA), hierarchical cluster analysis (HCA), Correlation coefficient and health risk analysis to find the common pollution source.

Results: The results for mean abundance during two seasons for cations and anions were 7 and 6.9 for pH; 1875 and 1527 for TDS; 3 and 3.3 (µs/cm) for EC; 655 and 569 for Ca^{2+}; 59 and 56 for Mg^{2+}; 340 and 211 for Na^{+}; 5 and 4 mg/L for K^{+}; 148 and 126 for CO_3^{2-} 301 and 228 for HCO_3^{-}; 289 and 223 for Cl^{-} 0.5 and 0.85 for F^{-}; 99 and 86 for SO_4^{2-} 28 and 23 mg/L for NO_3^{-}. While for heavy metals 18 and 4 for As; 2 and 0.4 for Cd; 29 and 5 for Cr; 17 and 4 for Cu; 25 and 6 for Ni; 82 and 3 for Pb; 953 and 989 µg/L for Zn, respectively. FA identified six dominant factors for each during summer and winter seasons that explained 70.43% and 71.06% of the variance in the dataset. Health risk assessment of chronic daily intake (CDI) and hazard quotient (HQ) during both seasons were in the order $Ca > Na > HCO_3 > Cl > CO_3 > SO_4 > Mg > NO_3 > K > F$ and was as well computed.

Conclusion: The significant reasons for water quality degrading in the study area were associated with various natural and anthropogenic sources and their unsystematic apportionment, show that proper land uses, industrial planning, design some remedial techniques and implementation of existing laws to have active groundwater resource management.

Keywords: Water quality, Groundwater, Contamination, Multivariate analysis, Risk assessment

Background

Water quality evaluation and administration are issues profoundly affecting human life. Particularly, the groundwater quality in a district is to a great extent influenced both by common procedures (geological interventions, weathering and soil disintegration) and by anthropogenic source (man-made, industrial and civil waste release). The industrial waste release constitutes a steady contaminating source, while surface overflow is a regular phenomenon (Kazi et al. 2009; Singh et al. 2004; Vega et al. 1996). Regular seasonal precipitation, surface run-off, groundwater stream and deliberation emphatically influence groundwater quality and subsequently on the concentration of toxins in water.

Broad analyses have been done on anthropogenic pollution of biological system by Niemi et al. 1990; Szymanowska et al. 1999; Krishna et al. 2009 and Issa et al. 1996. They have reported human activities are a major

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deciding factor in determining the nature of surface and groundwater through atmospheric contamination, effluent releases, utilization of farming chemicals like pesticides, dissolved soils and land utilize. Additionally, several recent studies on groundwater quality have been conducted (e.g., Chen et al. 2016; Cao et al. 2016) wherein they have concluded that agriculture activities, unplanned municipal development and insufficient hydrochemical knowledge are some factors responsible for poor groundwater quality. In recent years, overexploitation and irresponsible management of groundwater has resulted in many environmental problems such as groundwater table decline, and subsidence, and groundwater pollution (Xia 2002). Particularly, the small nations have been enduring this effect because of cluttered economic development related with the exploitation of natural resources (Kazi et al. 2009).

In various parts of India, especially in the dry and semi-dry areas, due to the driving forces of cyclones and deficiency of surface water, dependence on groundwater resources has extended gigantically in the progressing years. Furthermore, rapid growth in urban population, development of agriculture and industrial activities cause an intense increase in water consumption. In spite of the fact that the industrial utilization of water is small when contrasted with farming purposes, the transfer of modern effluents ashore/or surface water bodies and presence of micropollutants in the aquatic environment at different time scales makes water assets inadmissible for different purposes (Ghosh 2005; Buechler and Mekala 2005; Andreas et al. 2009). Nonetheless, because of spatial and temporal variations in water quality which gives a proxy and solid estimation of the groundwater quality is important (Dixon and Chiswell 1996). One such approach would be hydrochemical investigations of groundwater frameworks which have set overwhelming attention on variations in the physical and chemical qualities of groundwater in time and space. Similar research by Igibah and Tanko (2019) has been studied carried out in assessment of urban groundwater quality using piper trilinear and multivariate techniques, where agriculture is the most significant commercial activity affecting the changes in groundwater quality by anthropogenic activity.

A standard approach in groundwater hydrochemistry to interpret hydrochemical processes is to make scatter plots between parameters and to classify hydrochemical variables using various diagrams (ex., Piper, Wilcox diagram). Second is a high-level approach, and a valuable tool which incorporates the utilization of various multivariate statistical procedures (principal component analysis (PCA), factor analysis (FA), cluster analysis (CA) and correlation analysis) which help in understanding the complex information of water quality and regular status of the investigation zone. In this context various water quality monitoring programs based on statistical tools using large dataset have also been applied for better understanding of quality and hydrochemistry of rivers (Renato et al. 2018; Christopher et al. 2019; Mrazovac and Miloradov-Vojinovi 2011). These methods further, permit the distinguishing proof of the possible sources that impact water systems and offer a significant tool for contamination issues and risk assessment-oriented characterisation of contaminated sites (Shrestha and Kazama 2007; Simeonov et al. 2003; Reghunath et al. 2002; Ammar et al. 2014; Carlon et al. 2001; Howladar et al. 2017).

The topography of the study area, a more seasoned alluvium makes it more immobilized to draining. Hence, more attention is needed to understand the processes happening in and around this particular industrial area. Hence, this systematic study was carried out with four primary objectives. (i) Of studying the impact of the industries on groundwater quality, (ii) recognizing the hydrochemical forms identified with groundwater quality, (iii) to decide and portray the fundamental procedures influencing, groundwater quality utilizing an assortment of multivariate statistical methods and (iv) risk assessment due to physicochemical constituents utilizing health risk parameters like chronic daily intake (CDI) and hazard quotient (HQ) were evaluated to study their impact on human health.

Materials and methods

Study area

The proposed study area known as Katedan Industrial Development Area (KIDA) is located south of Hyderabad city on Hyderabad—Bangalore National Highway (NH 7). Around 300 industries are producing, edible oil, battery fabricating, metal plating, metal amalgams, plastic items, synthetic substances, and so forth, are situated in the area. These industries were arranged under small, medium and extensive scale industries. It is seen that most of the industrial parts, chiefly release their effluents into the streams and the solid waste created is discretionarily dumped on open land along lanes and lakes (Govil et al. 2012; Krishna and Mohan 2014).

The study area under examination falls in the semi-arid-dry zone, and the event of the initial spell of rainfall is amid June. Figure 1 demonstrates the magnitude of the study area (KIDA) encompassing residential and industrial zones separated. The industrial zone is isolated from the downstream residential locations by the railroad and an interstate expressway. The soil cover is an all-around well-developed persistent soil of weathered granite with porous and the invasion rate that can assimilate the vast majority of the rain aside from more extreme downpours. The lithological units comprise of granites and pegmatite of volcanic source having a place with the Archaean age. The granites are pink and dark, hard huge to foliated and very much jointed. Epidote and Quartz veins crosscut the granites at different spots. These rocks have minute porosity however are rendered with a porosity and penetrability because of secondary porosity by profound fractures and weathering, which locally shape potential aquifers. Water level varies every year in all the bore wells and usually rise in winter season with the water table fluctuating between 1 and 15 m below ground level and during summer season water levels often decline, and the water table fluctuates between 10 and 25 m.

Sampling and preparation

A total of one hundred and twenty (120) groundwater samples were collected from the study area out of which 60 samples during summer and 60 samples during the winter season (Fig. 1), which covers groundwater samples from bore wells, hand pumps and dug wells comprising of 98 bored and furnished with electric submersible pumps, 15 drilled and outfitted with hand pumps and 7 dug wells. The greater part of the wells outfitted with submersible pumps are essentially utilized for industrial purpose but yet many are additionally utilized for domestic reason. The capability of the wells isn't known yet the electric wells keep running for 3 to 8 h every day and the hand pumps are consistently being utilized. Location and list of well inventory data are shown in Table 1.

Water samples were collected in one litre size polythene bottles from demonstrative bore wells/burrowed wells/hand pump spread throughout the study area which are under use amid both summer and winter seasons. The sample containers were altogether washed with diluted acid and after that with distilled water in the lab. Before filling the samples, the container was flushed to keep away from any possible contamination. On location observations like area, source, pH, TDS and depth of the bore well were noted in the field notes. The water sample was then sifted and acidified (2 mL of HNO_3) to each 100 mL of the sample and was measured for heavy metals by ICP-MS.

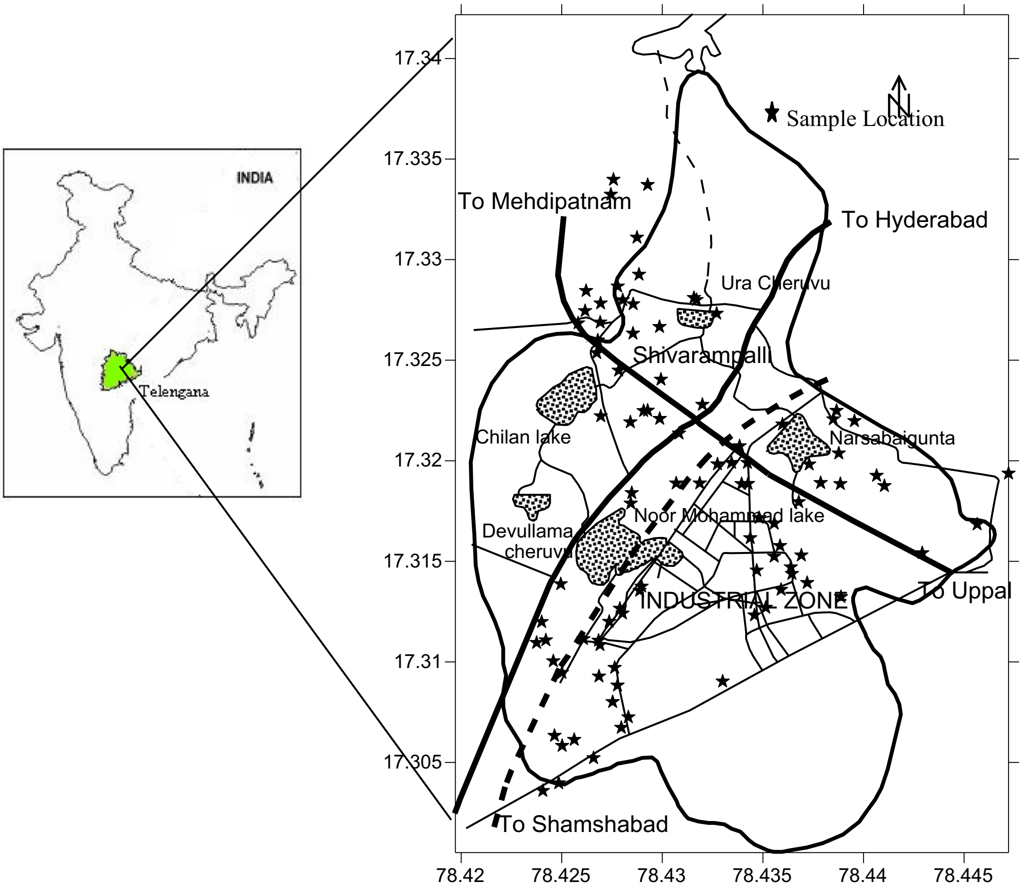

Fig. 1 Study area and sample location map

Table 1 Summary of well inventory data in the study area

S no.	Well-ID	Elevation in meters	Type of well	Depth of well in meters	No. of years in use	Purpose	Use per day (h)
1	GW 5	1798	Bore well	120	7	Industrial	3
2	GW 6	1824	Bore well			Industrial	3
3	GW 7	1808	Bore well	400	3	Industrial	2
4	GW 8	1805	Bore well	120	10	Industrial	5
5	GW 9	1833	Bore well	380	7	Industrial	24
6	GW 10	1830	Bore well	380	4 months	Industrial	1
7	GW 11	1823	Bore well	180	6	Industrial/domestic	4
8	GW 12	1835	Bore well	300	2	Industrial	2
9	GW 13	1852	Bore well			Industrial	1
10	GW 14	1862	Bore well	300	3	Industrial	1
11	GW 15	1845	Bore well	200	15	Industrial/domestic	3
12	GW 16	1811	Bore well	160	5	Industrial	1
13	GW 17	1834	Bore well	150		Industrial	1
14	GW 18	1838	Bore well	300	6	Industrial	21/2
15	GW 19	1842	Bore well			Industrial	21/2
16	GW 20	1868	Bore well	210	8	Industrial	18
17	GW 21	1845	Bore well	250	2	Industrial	
18	GW 22	1830	Bore well			Industrial/domestic	2
19	GW 23	1821	Bore well		7	Industrial/domestic	8
20	GW 24	1830	Bore well	160	4	Industrial	1
21	GW 25	1824	Bore well	300	2	Industrial	3
22	GW 26	1832	Bore well	300	3	Industrial	1
23	GW 27	1842	Bore well			Industrial	2
24	GW 28	1846	Bore well	150	3	Industrial	2
25	GW 29	1832	Hand pump	280	7	Industrial	
26	GW 30	1886	Dug well	30	Old		Not in use
27	GW 31	1825	Hand pump			Domestic	
28	GW 32	1815	Bore well	300	2	Domestic	5
29	GW 33	1798	Bore well	200	15	Industrial/domestic	2
30	GW 34	1795	Hand pump	200		Industrial	
31	GW 35	1793	Bore well		6	Industrial	1
32	GW 36	1800	Bore well	150	4	Industrial	3
33	GW 37	1805	Bore well	130	11	Industrial	3
34	GW 38	1800	Dug well	15			Not in use
35	GW 39		Bore well	350	5	Industrial	4
36	GW 39A		Bore well	350	5	Industrial	4
37	GW 40		Bore well	150	24	Industrial/domestic	1
38	GW 41	1812	Bore well	150	8	Industrial	1
39	GW 42	1812	Bore well	100	5	Industrial	1
40	GW 43	1774	Bore well	200	15	Industrial	Not in use
41	GW 44	1724	Bore well	150	15	Industrial	3
42	GW 45	1724	Bore well	150	15	Industrial	5
43	GW 46	1779	Bore well	200	14	Industrial	4
44	GW 47	1832	Hand pump			Domestic	
45	GW 48	1830	Bore well	60	4	Industrial	3
46	GW 49	1834	Bore well	180	20 days	Industrial	2
47	GW 50	1826	Bore well			Industrial	3
48	GW 51	1839	Hand pump	100	15	Domestic	
49	GW 52	1838	Bore well	150	2	Industrial	

Table 1 (continued)

S no.	Well-ID	Elevation in meters	Type of well	Depth of well in meters	No. of years in use	Purpose	Use per day (h)
50	GW 53	1847	Bore well			Industrial	10
51	GW 54	1856	Bore well	150	18	Industrial	4
52	GW 55	1860	Bore well	350	8	Industrial	17
53	GW 56	1866	Bore well	200	10	Industrial	Not in use
54	GW 57	1832	Bore well	280	3	Domestic	5
55	GW 58	1826	Bore well	300	7 months	Domestic	1
56	GW 59	1841	Bore well	300	2	Domestic	4
57	GW 60	1826	Bore well		5 months	Domestic	2
58	GW 61	1819	Hand pump	400	1	Industrial	
59	GW 62	1809	Bore well	150–200	10	Industrial	1
60	GW 63	1797	Bore well	393	2	Domestic	10
61	GW 64	1784	Bore well	200	5	Domestic	6
62	GW 65	1793	Bore well	400	31/2	Domestic	1
63	GW 66	1915	Bore well	400	3	Domestic	1
64	GW 67	1782	Bore well	410	3	Domestic	8
65	GW 68		Dug well	25	13	Domestic	
66	GW 69		Dug well	35	9	Industrial	
67	GW 70		Bore well	110	5	Domestic	1
68	GW 71	1799	Bore well	280	5	Industrial	2
69	GW 72	1835	Bore well	380	21/2	Domestic	8
70	GW 73	1814	Bore well	300	2 months	Domestic	2
71	GW 74	1870	Bore well	350	5	Domestic	8
72	GW 75	1800	Bore well	360	2	Domestic	8
73	GW 76	1814	Hand pump	180	3	Domestic	
74	GW 77	1843	Bore well	105	8	Domestic	2
75	GW 78	1842	Bore well	150	8	Domestic	1
76	GW 79		Bore well		8	Domestic	1
77	GW 80	1763	Hand pump	150	4	Domestic	
78	GW 81	1787	Bore well			Domestic	8
79	GW 82	1785	Hand pump	170	10	Domestic	
80	GW 83	1787	Bore well	150	11	Domestic	1
81	GW 84	1781	Bore well	100	5	Domestic	1
82	GW 85	1854	Bore well	150	2	Domestic	5
83	GW 86	1746	Bore well	150–200	2	Domestic	1
84	GW 87	1750	Bore well	> 200	10	Industrial/gardening	6
85	GW 88	1786	Bore well	150	15	Poultry/domestic	2
86	GW 89	1748	Dug well	56		Irrigation	Not in use
87	GW 90	1868	Bore well	200	20	Industrial	3
88	GW 91	1816	Bore well			Domestic	6
89	GW 92	1800	Hand pump	200	2	Domestic	
90	GW 93	1819	Hand pump	100–150	4	Domestic	
91	GW 94	1803	Hand pump	150	12	Domestic	
92	GW 95	1781	Bore well	165	7	Industrial	3
93	GW 96	1797	Bore well	100	10	Industrial	1
94	GW 97	1820	Bore well	140	4	Industrial	1
95	GW 98	530 m	Bore well			Industrial	2
96	GW 99	541 m	Bore well		2	Domestic	18
97	GW 100	542 m	Bore well		20	Domestic	8
98	GW 101	543 m	Bore well	160	1	Domestic	1

Table 1 (continued)

S no.	Well-ID	Elevation in meters	Type of well	Depth of well in meters	No. of years in use	Purpose	Use per day (h)
99	GW 102	546 m	Hand pump	110	5	Domestic	
100	GW 103	545 m	Bore well	180	3	Domestic	1
101	GW 104	538 m	Bore well	140	5	Domestic	1
102	GW 105	547 m	Bore well	50	8 months	Domestic	1
103	GW 106	538 m	Bore well	120	1	Domestic	1
104	GW 107	536 m	Bore well	100	1	Domestic	1
105	GW 108	530 m	Bore well	180	6 months	Domestic	2
106	GW 109	539 m	Bore well			Domestic	2
107	GW 110	529 m	Bore well			Domestic	5
108	GW 111	529 m	Bore well	160	6	Domestic	1
109	GW 112		Bore well	300	15	Domestic	16
110	GW 113	527 m	Hand pump	120		Domestic	
111	GW 114	528 m	Dug well				Not in use
112	GW 115		Bore well	110	6	Domestic	2
113	GW 116	552 m	Bore well	100	15	Domestic	2
114	GW 117	559 m	Bore well	100	15	Domestic	3
115	GW 118	556 m	Bore well	100	15	Domestic	5
116	GW 119	544 m	Bore well			Domestic	4
117	GW 120	587 m	Dug well	55	15		Not in use
118	GW 121	550 m	Bore well	240	3 months	Industrial	2
119	GW 122	534 m	Dug well	50	7	Irrigation	
120	GW 123	521 m	Bore well	110	5	Irrigation	

Analytical procedures and instrumentation

In light of broad analysis, 20 parameters were measured utilizing prescribed strategies for investigation (APHA 1995) for physicochemical parameters and significant metals which was incorporated into the list of criteria concerning the quality of water (Table 2). Measurements were done for pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), carbonate ($CO_3{}^{2-}$), hydrogen carbonate ($HCO_3{}^{-}$), chloride (Cl^{-}), sulfate ($SO_4{}^{2-}$) and nitrate ($NO_3{}^{-}$) according to standard strategies (APHA 1995). Electrical conductivity measurements are expressed in micro siemens/cm at 25 °C, the concentrations of cations and anions are expressed in mg/L and for heavy metals in µg/L. Sodium and potassium by inductively plasma mass spectrometer (ICP-MS), calcium, magnesium, total dissolved solids, and alkalinity by titrimetric methods, sulphates, and nitrates by ion-selective electrodes. Heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) were examined by ICP-MS. The instrument used for heavy metal measurements was Plasma Quad (VG Elemental Ltd., Winsford, Cheshire, UK). Calibration curves were prepared using multielement standard solution after dilution to micrograms per litre levels. The accuracy and precision (QC/QA) of the analysis was compared with reference water samples 1643b from National Institute of Standards and Technology (NIST, USA) which was used to check the reliability of calibration curve. All heavy metal results were obtained in the multielement mode and the samples were prepared in triplicates and analysed twice. The values obtained by ICP-MS are in close agreement with recommended values, the precision are better than 2% and show comparable accuracy (Table 3).

Data treatment and multivariate statistical methods

Groundwater data for summer and winter season was subjected to multivariate statistical methods regarding distribution and correlation among the studied parameters. The location of water sampling was recorded utilizing an Atrax display global positioning system (GPS) receiver framework. SPSS 10.0 programming platform (SPSS 1995) was utilized for statistical analysis of the information. Essential descriptive statistical parameters, for example, range, mean, standard deviation, kurtosis, and skewness were handled for both seasons (Table 4) correlation coefficient relationship analysis (Table 5), while multivariate measurements such as PCA and CA were also carried out. PCA was performed utilizing the varimax standardized rotation

Table 2 Standards and method of analysis

Test parameters	Symbol	Units	Description of standard analytical methods
Physical parameters			
pH	pH	pH units	pH meter
Total dissolved solids	TDS	mg/L	TDS meter
Electrical conductivity	EC	µs/cm	Conductivity meter
Major cations			
Calcium	Ca^{2+}	mg/L	Titrimetric
Magnesium	Mg^{2+}	mg/L	Titrimetric
Sodium	Na^{+}	mg/L	ICP-MS
Potassium	K^{+}	mg/L	ICP-MS
Major anions			
Carbonate	CO_3^{2-}	mg/L	Titrimetric
Bi-carbonate	HCO_3^{-}	mg/L	Titrimetric
Chloride	Cl^{-}	mg/L	Titrimetric
Fluoride	F^{-}	mg/L	Calorimetric
Sulphate	SO_4^{2-}	mg/L	ISE
Nitrate	NO_3^{-}	mg/L	ISE
Heavy metals			
Arsenic	As	µg/L	ICP-MS
Cadmium	Cd	µg/L	ICP-MS
Chromium	Cr	µg/L	ICP-MS
Copper	Cu	µg/L	ICP-MS
Nickel	Ni	µg/L	ICP-MS
Lead	Pb	µg/L	ICP-MS
Zinc	Zn	µg/L	ICP-MS

Table 3 Heavy metal data for water reference sample NIST 1643b by ICP-MS (Krishna and Mohan 2014)

Analyte	ICP-MS value (µg/L)	Recommended value (µg/L)	Average (RSD%)
As	50.29	49.0	1.81
Cd	19.89	20.0	0.39
Cr	18.72	18.6	0.45
Cu	21.69	21.9	0.68
Ni	47.87	49.0	1.67
Pb	24.02	23.7	0.94
Zn	66.89	66.0	0.94

on the data, and the CA was linked to the sample concentrations utilizing dendrogram strategy (Liu et al. 2003; McKenna 2003; Omo-Irabor et al. 2008). These principal components give data on the most important parameters which depict the entire dataset bearing information on data reduction with least loss of unique data. PCA is an effective method for pattern recognition that attempts to explain the difference of an expansive arrangement between related factors and changing into a smaller arrangement of autonomous (uncorrelated) variables (principal components). In this study, hierarchical agglomerative CA was performed on the normalized dataset employing Ward's method, using square Euclidean distances as a measure of similarity.

Human health risk assessment

The identification and characterization of associated human health risks is based on integrating factors such as ecotoxicology and physico-chemical analysis, of the dangerous metals on individuals through direct ingestion, inward breath through mouth and nose, dermal assimilation through skin introduction have been considered (Donkor et al. 2015; Sophie et al. 2011).

In the present study, we have adopted the same equations and calculated based on the concentrations of cations and anions to calculate the health risk assessment utilizing chronic daily intake (CDI) and hazard quotient (HQ) indices. The CDI through water ingestion was figured utilizing the condition by USEPA (1992) underneath:

$$\mathrm{CDI} = \mathrm{C} \times \mathrm{DI}/\mathrm{BW} \tag{1}$$

where C, BW represents the concentration of cation/anion in groundwater (mg/L), average daily intake rate (2 L/day) and body weight (72 kg), respectively (USEPA 2005). On the other hand, the chronic risk level was calculated (HQ) for non-carcinogenic risk using following equation by USEPA (1999):

$$\mathrm{HQ} = \mathrm{CDI}/\mathrm{RfD} \tag{2}$$

where according to USEPA, the oral toxicity reference dose values (RfD) are 41.4 mg/kg-day for Ca, 11.0 mg/kg-day for Mg; 1.0 for K, 0.067 mg/kg-day for Cl 0.06 mg/kg-day for F, and 1.6 mg/kg-day for NO_3 respectively (USEPA 1989). The scale of chronic risk level (HQ) based on average daily intake (CDI) and reference dose (mg/kg-day) is classified based on the ratio of CDI/RfD indicating ≤ 1 (no risk) if $> 1 \leq 5$ (low risk), if $> 5 \leq 10$ (medium risk), if > 10 (high risk).

Results and discussion

Descriptive statistics of 20 physicochemical parameters of groundwater in the study area during summer and winter seasons are summarized in Table 4. In summer groundwater samples indicated, pH (6.4–8.1) moderately acidic to alkaline while TDS and conductivity vary from 620 to 4361 mg/L and 1.0 to 7.6 µs/cm. Mean cation occur in the order of $K < Mg < Na < Ca$, anion concentrations arise in the order of $F < NO_3 < SO_4 < CO_3 < Cl < HCO_3$ and heavy metals occur in the order $Cd < As < Ni < Cu < Cr < Pb < Zn$. In winter, groundwater showed, pH (6.4–7.8) acidic to mild alkaline while TDS and conductivity vary

Table 4 Descriptive Statistics of groundwater quality during summer and winter seasons

Parameters	Units	Range (summer)	Mean	Std. deviation	Skewness	Kurtosis	Range (winter)	Mean	Std. deviation	Skewness	Kurtosis	WHO limit (2014)	Igbah and Tanko (2019) (mean)
pH	pH	6.4–8.1	7	0.4	0.8	0.7	6.4–7.8	6.9	0.3	0.7	0.9	6.5–8.5	6.75
TDS	mg/L	620–4361	1875	819	1.0	0.7	445–2829	1527	552	0.5	−0.2	1000	1068
EC	µs/cm	1.0–7.6	3	1	0.7	0.5	1.11–7.25	3.3	1	0.7	0.11	1500	1796
Ca^{2+}	mg/L	88–2477	655	430	1.8	5.2	84–1584	569	316	0.9	0.8	300	66.6
Mg^{2+}	mg/L	2.0–286	59	69	2.0	3.5	2.3–256	56	62	1.8	3	50	83.4
Na^{+}	mg/L	31.0–1012	340	253	1.1	0.2	27–563	211	133	1	0.7	50	260
K^{+}	mg/L	0.6–21	5	3.3	3.0	12	1.10–9	4	2	0.8	1.3	12	6.15
CO_3^{2-}	mg/L	32–321	148	65	1.0	0.2	30–269	126	54	1	0.7	NA	19.5
HCO_3^{-}	mg/L	66–765	301	189	1.0	0.0	63–765	228	123	2	5	500	481
Cl^{-}	mg/L	84–1181	289	187	2.4	9.2	35–896	223	132	3	12	250	236
F^{-}	mg/L	0.10–1.20	0.5	0.3	1.0	0.3	0.09–23	0.85	3	7	51	1.5	1.28
SO_4^{2-}	mg/L	9.2–493	99	86	2.5	8.4	6.3–305	86	66	2	3	250	447
NO_3^{-}	mg/L	6.0–75	28	16	0.7	0.1	4.4–66	23	14	1	0.5	50	4.20
As	µg/L	1.0–62	18	19	1.1	−0.3	1.09–12	4	2	2	5	10	
Cd	µg/L	0.20–7	2	1.5	2.0	4	0.04–6	0.4	1	5	19	5	
Cr	µg/L	6.4–217	29	32	4.3	25	0.47–10	5	3	−0.2	−1.6	50	
Cu	µg/L	1.4–200	17	29	5.3	32	0.92–18	4	3	2	6	2000	
Ni	µg/L	1.2–76	25	19	1	−0.3	0.11–38	6	7	3	7	70	
Pb	µg/L	0.4–454	82	102	2	3	0.09–45	3	7	5	27	10	
Zn	µg/L	34–5818	953	1091	2	7	16–22036	989	4241	5	23	3000	

Table 5 Correlation coefficient (r) matrix of cations, anions and selected metals in groundwater during summer season (above the diagonal) and winter season (below the diagonal; n = 120)

	As	Ca^{2+}	Cd	Cl^-	CO_3	Cr	Cu	EC	F^-	HCO_3^-
As	1.00	0.91**	0.02	0.86**	0.25	0.00	0.36	0.70	0.36	0.27
Ca^{2+}	0.82**	1.00	0.23	0.00	0.01	0.57	1.00	0.14	0.26	0.00
Cd	0.98**	0.44	1.00	0.17	0.15	0.00	0.46	0.34	0.34	0.02
Cl^-	0.13	0.00	0.88**	1.00	0.00	0.96**	0.44	0.00	0.55	0.00
CO_3	0.62*	0.00	0.81**	0.00	1.00	0.33	0.25	0.00	0.36	0.00
Cr	0.86**	0.06	0.02	0.38	0.90**	1.00	0.69*	0.94**	0.69*	0.25
Cu	0.00	0.44	0.08	0.15	0.59	0.80**	1.00	0.68*	0.68*	0.15
EC	0.61*	0.00	0.40	0.00	0.00	0.28	0.70**	1.00	0.02	0.00
F	0.20	0.61*	0.77**	0.45	0.04	0.31	0.20	0.01	1.00	0.65*
HCO_3^-	0.13	0.01	0.72**	0.00	0.00	0.79**	0.33	0.00	0.35	1.00
K^+	0.03	0.40	0.45	0.09	0.24	0.85**	0.04	0.64*	0.46	0.42
Mg^{2+}	0.46	0.01	0.67*	0.01	0.00	0.58*	0.03	0.00	0.06	0.02
Na^+	0.40	0.02	0.20	0.12	0.52	0.63*	0.52	0.04	0.09	0.05
Ni	0.00	0.57	0.03	0.06	0.97**	0.30	0.00	0.79**	0.01	0.64*
NO_3^-	0.04	0.20	0.84**	0.02	0.01	0.70**	0.56	0.00	0.20	0.00
Pb	0.88**	0.50	0.00	0.23	0.96**	0.00	0.00	0.36	0.13	0.68*
pH	0.78**	0.07	0.28	0.09	0.04	0.76**	0.79**	0.23	0.28	0.07
SO_4^{2-}	0.37	0.02	0.74**	0.72**	0.42	0.26	0.63*	0.52	0.44	0.37
TDS	0.49	0.00	0.38	0.00	0.00	0.25	0.35	0.00	0.15	0.00
Zn	0.64*	0.21	0.00	0.84**	0.49	0.54	0.33	0.46	0.61*	0.35

	K^+	Mg^{2+}	Na^+	Ni	NO_3^-	Pb	pH	SO_4^{2-}	TDS	Zn
As	0.29	0.99**	0.67*	0.00	0.62*	0.01	0.21	0.59	0.43	0.00
Ca^{2+}	0.38	0.12	0.03	0.51	0.10	0.02	0.10	0.26	0.00	0.88**
Cd	0.64*	0.27	0.54	0.32	0.04	0.00	0.66*	0.85**	0.04	0.00
Cl^-	0.61	0.00	0.06	0.74**	0.01	0.23	0.26	0.34	0.00	0.95**
CO_3	0.24	0.02	0.68*	0.97**	0.01	0.32	0.00	0.38	0.00	0.64*
Cr	0.30	0.71**	0.78**	0.28	0.33	0.00	0.60*	0.99**	0.75**	0.00
Cu	0.00	0.90**	0.44	0.03	0.72**	0.18	0.54	0.53	0.32	0.58
EC	0.02	0.00	0.03	0.65*	0.01	0.05	0.01	0.65*	0.00	0.86**
F	0.35	0.65*	0.58	0.73**	0.43	0.55	0.01	0.44	0.83**	0.53
HCO_3^-	0.08	0.17	0.22	0.47	0.01	0.02	0.01	0.92**	0.00	0.41
K^+	1.00	0.12	0.98**	0.84**	0.71**	0.44	0.20	0.72**	0.18	0.29
Mg^{2+}	0.11	1.00	0.78**	0.97**	0.02	0.17	0.40	0.71**	0.02	0.89**
Na^+	0.39	0.36	1.00	0.62*	0.19	0.15	0.49	0.88**	0.00	0.11
Ni	0.83**	0.97**	0.09	1.00	0.96**	0.10	0.43	0.99**	0.50	0.09
NO_3^-	0.32	0.00	0.15	0.56	1.00	0.06	0.75**	0.61*	0.00	0.59
Pb	0.04	0.36	0.63*	0.00	0.54	1.00	0.76**	0.64*	0.00	0.00
pH	0.16	0.82**	0.17	0.67*	0.76**	0.87**	1.00	0.31	0.03	0.35
SO_4^{2-}	0.20	0.61*	0.97**	0.83**	0.41	0.23	0.08	1.00	0.94**	0.66*
TDS	0.14	0.00	0.00	0.85**	0.00	0.79**	0.05	0.99**	1.00	0.42
Zn	0.67*	0.34	0.37	0.46	0.52	0.98**	0.31	0.26	0.60	1.00

n number of groundwater samples

*Level of significance = 0.05

**Level of significance = 0.01

from 445 to 2829 mg/L and 1.0 to 7.3 µs/cm. Mean cation and anion concentrations were found to be abundant in the order $K < Mg < Na < Ca$ and $F < NO_3 < SO_4 < CO_3 < Cl < HCO_3$, whereas heavy metals occurred in the order $Cd < Pb < As < Cu < Cr < Ni < Zn$. The chemical composition of analyzed groundwater samples of the study area is represented by plotting them in the Piper tri-linear diagram for summer and winter seasons (Fig. 2a, b). These diagrams reveal the distribution of the groundwater samples in different subdivisions of the diamond-shaped field of the piper diagram, the analogies, and dissimilarities. The results obtained in this study were compared with the studies by Igibah and Tanko (2019) where results revealed that the water quality parameters showed wide spatial variations in the order $Na^+ > SO_4^{2-} > EC > Mg^{2+} > TDS > Fe^{2+} > HCO^{3-} > F^- > TH > Cl^-$, ensuing groundwater contamination from weathering, agriculture and anthropogenic activities

Water quality assessment

The ion concentration distribution as displayed on the piper-diagram, where the trilinear diagrams illustrated the relative concentrations of cations and anions. During summer, it is found that 95% of the groundwater is falling in the field 1, 5% in the field 2, 13% in the field 3, 88% in the field 4, whereas 10% of the groundwater in the field 5 including secondary alkalinity. 25% of the area falls in the field 6, under secondary salinity. 11% of the groundwater falls in the field 7 indicating primary salinity and nil, in the field 8 indicating no primary alkalinity. It is witnessed that the entire area is devoid of alkaline earth and secondary salinity. During winter, it is found that 95% of the groundwater is falling in the field 1 and 5% and 10% of the groundwater is falling in the fields 2 and 3. 90% falls in the field 4 of strong acids exceed weak acids, whereas 10% of the groundwater in the field 5 including secondary alkalinity. 28% of the groundwater samples fall in the field 6 of secondary salinity. 4% of the groundwater falls in the field 7 indicating primary salinity and 57% in the area stating that no cation and anion exceeds 50%. The cations, particularly Ca, Mg and Na, concentrations during winter are almost same as during summer, due to which there is no major difference in the percentage of samples falling in field 1 in piper diagram. It is presumed that there is no significant dilution of cationic and anionic concentrations of almost all samples during winter compared to summer. The geochemistry of subsurface waters is affected by reactions with host rocks. Bi-carbonate (HCO_3^-) is the dominant ion in most subsurface waters. The well water may be the principle source of drinking water for the majority of communities in the third world countries, as well as for small, remote communities or

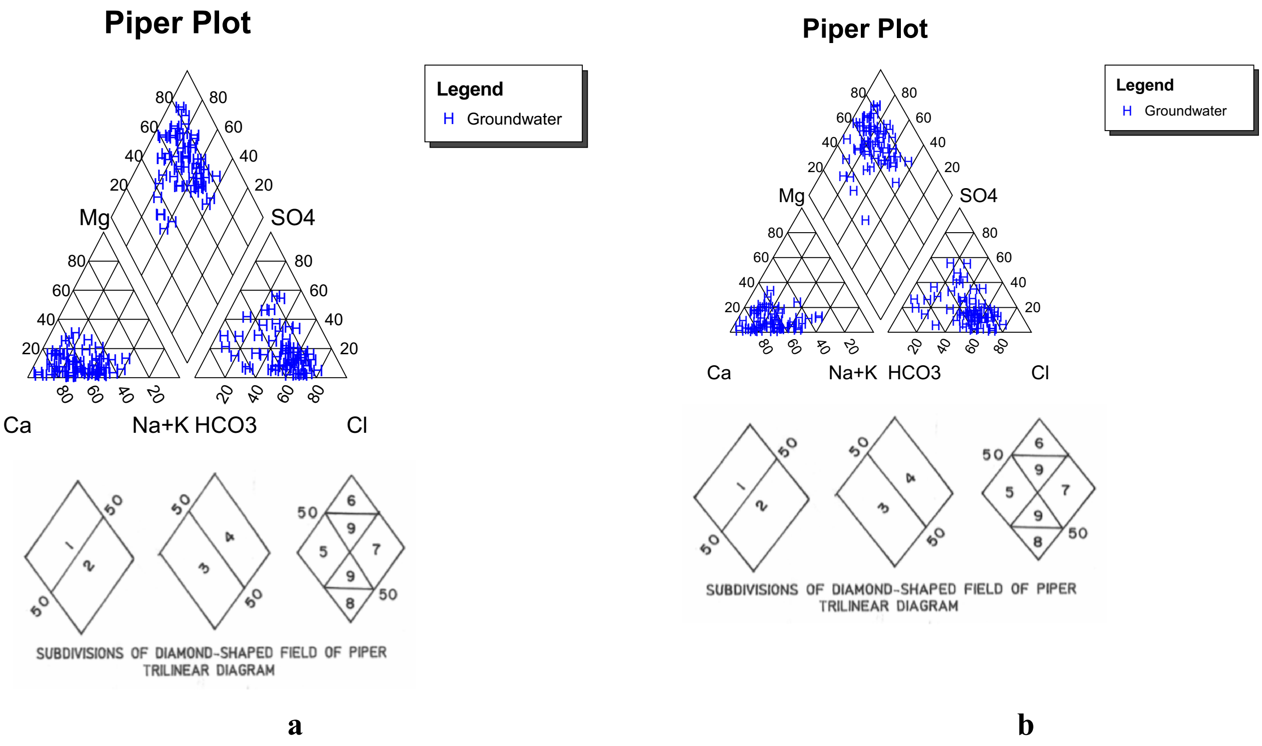

Fig. 2 Piper trilinear diagram representing the chemical analysis during summer (**a**) and winter (**b**) season

homesteads in the industrialized countries. It is necessary to understand the relationship between the rock type and chemical characteristics of water. The nature of water is of indispensable concern for humankind since it is specifically connected with human welfare. It is presently for the most part perceived that the nature of groundwater accessible in a region is as essential as the quantity.

Correlation of physicochemical parameters

Correlation coefficients between 20 representative chemical parameters were calculated for both summer and winter seasons and displayed in Table 5. The importance of the linear relationship between variables is determined by coefficients in the (− 1, 1) interval. The connection between two factors is the relationship coefficient ('r') which indicates how one variable predicts the other. A high correlation coefficient (near 1) means a good relationship between two variables, and a correlation coefficient around zero indicates no relationship. Positive values of 'r' indicate a +ve relationship while −ve values indicate an inverse relationship. The results in this study show different types of correlation, stronger positive, weak positive and negative type of correlation coefficient. The highest correlation ($r > 8.0$) is noticed during summer, Ca–As; Cl–As; Cr–Cl; Cu–Ca; EC–Cr; Mg–As, Cu; Na–K; Ni–CO_3, Mg; SO_4–Cd, Cr, HCO_3, Na, Ni; and during winter Ca–As; Cd–As; CO_3–Cd; Cr–As, CO_3, K; NO_3–Cd; Ni–CO_3, K, Mg; Pb–As, CO_3; SO_4–Na, Ni; TDS–Ni, SO_4; Zn–Cl, Pb.

High and significant correlations between cations, anions and metals indicate that contaminants in the study area (KIDA) waters have a similar source which originates from industrial activities.

Principal component/factor analysis

Factor analysis was performed for the samples during summer and winter by the extraction method (principal component analysis). The rotation of the principal components was executed by the Varimax method with Kaiser normalization. The outcome of the PCA based on the correlation matrix of chemical components for summer and winter seasons are expressed in Table 6. Six components of PCA analysis showed 70.43% of the variance in the summer data set of the study area. The eigenvectors classified the 20 physicochemical parameters including heavy metals into six groups. The first component (VF1) is loaded with cations and anions; the second component (VF2) is loaded with trace and toxic metals, while third, fourth and fifth components (VF3, VF4, VF5) shows F, Cu and SO_4 and sixth component (VF6) was not significant. Whereas, for winter data set the six components of PCA analysis showed 71.06% of the variance for 20 physicochemical parameters into six groups. The first component (VF1) is loaded with major elements (Ca, Cl, CO_3, Mg, and TDS)' the second component (VF2) is loaded with trace and toxic metals. While third, fourth, fifth components (VF3, VF4, VF5, V6) are loaded with major and toxic metals.

To select wells with a natural content of heavy metals, free of anthropogenic contamination, filled with uncertainties especially when some wells of little contamination were also inside the industrial area. A statistical interpretation of all the summer chemical well data improved the understanding of the chemical well characteristics. The results of the factor analysis as shown in Fig. 3 clearly indicate the increasing anthropogenic contamination. From a small cluster to the left of uncontaminated wells the contamination is increasing to the right, first in wells with contamination of individual heavy metals and further to the right wells, multi-contamination of heavy metals.

Factor 1 during summer and winter seasons represented 25.35% and 23.38% of the aggregate difference and was essentially made out of positive loading (Ca^{2+}, Cl^- $CO_3{}^{2-}$, EC, TDS and $HCO_3{}^-$). The positive content of Ca demonstrated the factors relationship with water–rock interaction as Ca^{2+} in groundwater essentially originates from the disintegration of carbonate. The Cl-might be derived from the contamination sources, for example, effluents of industrial and domestic composts and septic tanks (Bohlke and Horan 2000; Widory et al. 2004; Valdes et al. 2007) and common sources, for example, precipitation, the suspension of liquid considerations and Cl-bearing minerals. The high positive stacking of EC and negative stacking of pH supported the hypothesis of water–rock interaction. The electrical conductance imitates the measure of material dissolved in groundwater and pH estimation of the groundwater imitates the H+ particle focus. The higher positive stacking of EC and TDS esteems are a marker of higher ionic concentrations, likely because of the high anthropogenic events in the study area and geological weathering condition.

The study area is most densely populated with both industrial and residential area and consequently witness higher groundwater abstraction. The nearby anthropogenic activities could be released from intensive and drawn out farming activities which present ions and metals from composts and different agrochemicals (Laar et al. 2011; Dinka et al. 2015). TDS estimate of > 500 mg/kg during the two seasons shows the nearness of marginally hoisted groupings of salts and is identified with different issues, for example, hardness (Herojeet et al. 2013). The dominance and source of CO_3 and HCO_3 in the study area may be attributed to the dissolved CO_2 in rainwater which dissolves as both CO_3 and HCO_3 ions

Table 6 Loading for varimax rotated factor matrix during summer and winter of six-factor model explaining 70.43% of the total variance for groundwater during summer season

Parameters (summer)	VF 1	VF 2	VF 3	VF 4	VF 5	VF 6	Parameters (winter)	VF 1	VF 2	VF 3	VF 4	VF 5	VF 6
As	−0.354	*0.661*	0.338	0.212	0.217	−0.159	As	−0.15	0.32	*0.78*	0.04	−0.05	0.05
Ca^{2+}	*0.618*	0.302	0.322	−0.122	−0.351	−0.229	Ca^{2+}	*0.61*	0.08	0.25	0.22	0.47	−0.09
Cd	−0.544	0.537	−0.122	−0.180	−0.179	0.052	Cd	−0.11	*0.74*	−0.09	−0.02	−0.01	−0.27
Cl^{-}	*0.669*	0.359	0.254	−0.009	−0.058	0.078	Cl^{-}	*0.69*	−0.13	0.05	0.19	0.10	−0.14
CO_3^{2-}	*0.675*	0.226	−0.238	−0.110	0.137	0.236	CO_3	*0.69*	−0.08	−0.03	−0.33	−0.02	−0.29
Cr	−0.353	*0.784*	0.001	−0.201	−0.023	0.019	Cr	0.08	0.03	−0.10	*0.83*	0.15	0.11
Cu	−0.179	0.144	−0.152	*0.760*	−0.280	−0.120	Cu	−0.19	0.51	0.16	−0.04	−0.02	0.19
EC	*0.681*	0.329	−0.298	0.155	0.244	0.074	EC	*0.79*	−0.09	0.07	0.11	−0.17	0.05
F	−0.091	−0.035	*0.703*	−0.011	−0.358	0.334	F	−0.03	−0.06	−0.10	0.13	*0.89*	−0.09
HCO_3^{-}	*0.787*	0.170	−0.093	−0.124	0.016	0.030	HCO_3^{-}	*0.67*	−0.09	−0.16	−0.20	0.25	−0.21
K^{+}	0.298	0.028	−0.435	0.553	−0.344	−0.053	K^{+}	0.14	−0.13	*0.74*	0.00	−0.07	−0.24
Mg^{2+}	0.456	0.247	−0.002	0.272	−0.073	0.492	Mg^{2+}	*0.68*	−0.09	0.06	0.42	−0.23	0.17
Na^{+}	0.371	0.102	0.248	−0.052	0.265	−0.621	Na^{+}	0.31	0.07	0.51	−0.33	0.35	0.19
Ni	−0.198	0.441	0.158	0.510	0.393	−0.225	Ni	0.00	*0.81*	0.46	−0.07	−0.02	0.04
NO_3^{-}	−0.524	−0.092	−0.266	−0.239	−0.192	−0.337	NO_3^{-}	−0.61	0.11	0.20	0.19	0.21	−0.18
Pb	*−0.606*	0.469	−0.129	−0.065	−0.037	0.168	Pb	−0.03	*0.95*	−0.04	−0.05	−0.01	0.05
pH	−0.363	−0.269	0.587	0.303	0.182	0.202	pH	−0.14	−0.07	−0.07	0.10	−0.08	*0.87*
SO_4^{2-}	−0.019	−0.092	−0.122	−0.053	*0.646*	0.266	SO_4^{2-}	0.04	0.28	−0.31	−0.51	−0.12	0.47
TDS	*0.870*	0.293	0.202	−0.122	−0.082	−0.143	TDS	*0.87*	0.03	0.22	0.00	0.40	−0.04
Zn	−0.386	*0.781*	−0.117	−0.182	−0.038	0.132	Zn	−0.04	*0.94*	−0.03	0.08	0.02	−0.01
Eigen value	5.108	3.043	1.754	1.608	1.337	1.247	Eigen value	4.68	3.47	1.9	1.58	1.47	1.12
Loading%	25.539	15.214	8.725	8.040	6.683	6.235	Loading%	23.38	17.33	9.52	7.89	7.35	5.58
Cumulative%	25.539	40.753	49.477	57.517	64.201	70.436	Cumulative%	23.38	40.71	50.23	58.12	65.47	71.06

The level of significance in italics for ≤ 0.61 is 0.05

The level of significance in italics for ≥ 0.61 is 0.01

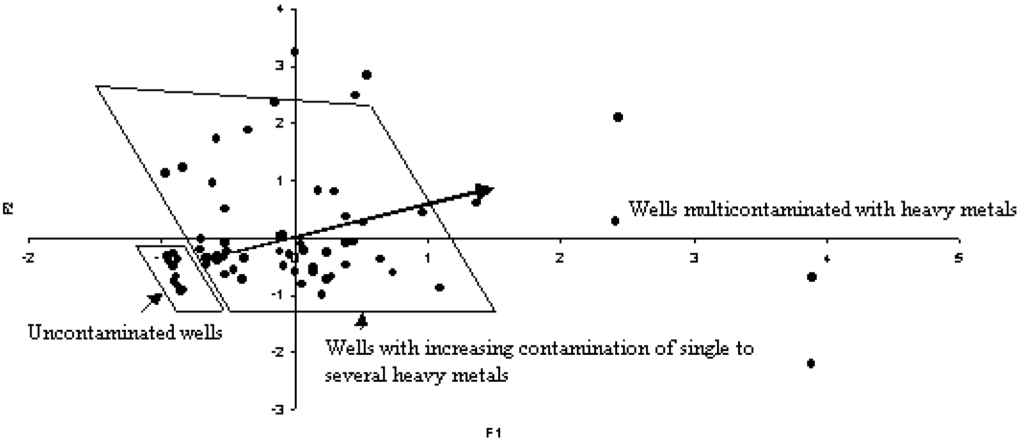

Fig. 3 Distribution of variables given by the factor analysis

when entered into the soil. Bouwer (1978) indicated that HCO_3 is mainly formed due to the action of CO_2 from the atmosphere and that, released from organic decomposition, accumulation of solid waste in industrial and sewage effluents. Therefore, factor 1 is assumed to be indicative of the contamination source related to human activity. Factor 2 explains during summer and winter seasons accounted for 15.21% and 17.33% of the total variance and was primarily composed of positive loading (As, Cr, Zn, Cd, Ni, and Pb). The data uncovers that these heavy metals have transported from surface water. As the study area is enveloped by granitic rocks, the spread of trace elements in granitic landscape is through fractures and joints which is extensively rapid than that in sedimentary arrangement.

The high loadings of Ni in winter may have impacted by nickel discharge into the air by scrap incinerators situated in a portion of the industries of the study area, which may have settled on surface water when it turns out to be a part of waste water streams as industrial effluents. The vast piece of all Ni aggravates that are released to the earth will ingest to deposits and end up stable (Krishna and Mohan 2014). Factor's 3, 4 and 5 during summer season accounted for 8.72%, 8.04% and 6.68% of the total variance with loadings of F, Cu, and SO_4. The high scores of SO_4 recorded explain the dissolution of sulfides such as pyrite from the interstratified materials by percolating into the water which produces SO_4 ions in water. Further, the salt water intrusion due to high TDS values in the study area is also probable source of the high SO_4 values. The Cu may be attributed to the anthropogenic activity due to industrial pollution. The positive loadings of factor's 3, 4, 5 and 6 with As, K, Cr, F, and pH during winter season accounted for 9.5%, 7.89%, 7.35%, 5.58% and 5.58% of the total variance. These loadings of K, F, pH and heavy metals can be attributed to the agriculture pollution and high salinity in the study area due to deposition of pesticides on to the surface soil, water and percolation into the groundwater aquifer system. Further, in a nutshell the results of PCA/FA can be presumed that in the study area the contamination of groundwater is mainly from agriculture run-off, soil weathering and run-off from solid waste, domestic and industrial wastewater disposal.

Cluster analysis

Cluster analysis involves a progression of multivariate strategies which are utilized to find right groups of information or stations. In clustering, the objects are grouped with the end goal that comparative articles fall into a similar class (Danielsson et al. 1999; Mrazovac et al. 2013). The hierarchical cluster analysis (CA) was applied utilizing Ward's strategy (linkage between groups), Euclidian separation as a similarity measure and synthesised in dendrograms. CA was performed on groundwater samples for both summer and winter seasons. The results are illustrated by dendrograms (Fig. 4a, b).

Dendrogram obtained for groundwater during summer (Fig. 4a) showed five clusters with Ca, TDS, Cl (Cluster I), CO_3, HCO_3, EC (Cluster II), Mg, Na, Cu, K (Cluster III), As, Ni, Cr, Zn, Cd, Pb (Cluster IV), NO_3, F, pH, SO_4 (Cluster V). Cluster I and II indicate the similar activity of factor 1; Cluster IV and V represent the same activity of factor's 2, 3, 4, 5 obtained by factor analysis during both summer and winter seasons. The following multielement factors were divided into factors with strong anthropogenic influence. Whereas, Cluster III represents the combined activity of factor 1 and factor 2. Similarly for groundwater, dendrogram obtained during winter (Fig. 4b) also showed five clusters with Pb, Zn, Ni (Cluster

```
                  a   Rescaled Distance Cluster Combine

  C A S E      0         5        10        15        20        25
Label     Num  +---------+---------+---------+---------+---------+

CA          2   -+-----------+
TDS        19   -+           +-----+
CL          4   -------------+     +-------+
CO3         5   -----------+-----+ I       I
HCO3       10   -----------+     +-+       +-----+
EC          8   -----------------+         I     +---------+
MG         12   ---------------------------+     I         +-----+
NA         13   ---------------------------------+         I     I
CU          7   -----------------------+-------------------+     I
K          11   -----------------------+                         I
AS          1   -----------+---------------+                     I
NI         14   -----------+               +---------+           I
CR          6   -+---------------+         I         I           I
ZN         20   -+               +---------+         +-------+   I
CD          3   ---------+-------+                   I       I   I
PB         16   ---------+                           I       +---+
NO3        15   -------------------------------------+       I
F           9   ---------------------------+---------------+ I
PH         17   ---------------------------+               +-+
SO4        18   -------------------------------------------+
```

```
                  b   Rescaled Distance Cluster Combine

  C A S E      0         5        10        15        20        25
Label     Num  +---------+---------+---------+---------+---------+

PB         16   -+---------+
ZN         20   -+         +-------+
NI         14   -----------+       +---------+
CD          3   -------------------+         +-----------+
CU          7   -----------------------------+           +-----+
AS          1   -----------------------------+-----+     I     I
K          11   -----------------------------+     +-----+     +-+
NA         13   -----------------------------------+           I I
CR          6   -------------------------------------+---+     I I
F           9   -------------------------------------+   +-----+ I
NO3        15   -----------------------------------------+       I
PH         17   ---------------------------------+---------------+
SO4        18   ---------------------------------+               I
EC          8   -----------------+---------+                     I
MG         12   -----------------+         +---------------------+
CO3         5   ---------------------+---+ I
HCO3       10   ---------------------+   +-+
CA          2   -----+---------------+   I
TDS        19   -----+               +---+
CL          4   ---------------------+
```

Fig. 4 Dendrogram of hierarchical cluster analysis in groundwater during Summer (**a**) and winter (**b**) season

I), Cd, Cu, As, K, Na (Cluster II), Cr, F, NO_3 (Cluster III), pH, SO_4, EC, Mg, CO_3, HCO_3 (Cluster IV), Ca, TDS, Cl (Cluster V). The cluster's I, II and III show the dominance of SO_4, Ca, Na, K, Mg, pH, and NO_3. TDS and moderate loadings on Na and K basically represents the solids group. This clustering points to common sources of natural process of disintegration of soil constituents primarily carbonates. It also represents the nutrients group of contaminants which points to some source of wastewater run-off. The level of Nitrates in water suggests human health and is a marker of the level of natural contamination of the water source (Donkor et al. 2015; Eletta et al. 2010; Gopalkrushna 2011; Mahananda et al. 2010). Therefore, the dominant source may be attributed to anthropogenic contamination from surrounding industries and release of effluents and domestic waste.

Human health risk assessment

It was observed that inhabitants in the study area were utilizing groundwater for different local and drinking purposes. Accordingly, encompassing water drinking sources from bore-wells and hand pumps which were utilized generally for local intentions were additionally chosen for substance parameters (cations/anions) risk evaluation like chronic daily intake (CDI) and hazard quotient (HQ) indices. The results of which are briefed in Table 7. The results in the study area recommend that, where individuals have used groundwater for residential utilization is gradually heading with expanded levels of hazardous elements and groundwater in a few sections that are not reasonable for drinking.

The CDI values for major cations and anions (Table 7) in groundwater during summer ranged from 2.44 to 68.9 for Ca, 0.06 to 7.94 for Mg, 0.86 to 28.1 for Na, 0.02 to 0.57 for K, 0.89 to 8.92 for CO_3, 0.86 to 21.2 for HCO_3, 0.32 to 32.8 μg/kg per day for Cl^{-}, 0.00 to 0.03 for F, 0.26 to 13.7 for SO_4 and 0.17 to 6.17 for NO_3 respectively. Whereas, during winter CDI values were ranging from 0.11 to 2.19 for Ca, 0.005 to 0.585 for Mg, 0.033 to 0.680 for Na, 0.001 to 0.006 for K, 0.024 to 0.249 for CO_3, 0.014 to 0.348 for HCO_3, 0.009 to 0.702 μg/kg per day for Cl^{-}, 0.00 to 0.034 for F, 0.004 to 0.177 for SO_4 and 0.002 to 0.052 for NO_3 respectively. Therefore, the order of toxicity in the form of CDI indices for major cations and anions based on mean concentrations for groundwater during summer and winter were found in the order of $Ca > Na > HCO_3 > Cl^{-} > CO_3 > SO_4 > Mg > NO_3 > K > F$. The high CDI values during summer may be attributed to anthropogenic activity the pesticide usage in agriculture fields wherein it is left into the streams as run-off from the fields.

Table 7 Chronic daily intake (CDI) and hazard quotient (HQ) indices for major cations and anions

Parameters	Statistics	Groundwater (CDI)		Groundwater (HQ)	
		Summer	Winter	Summer	Winter
Ca^{2+}	Min	2.44	0.11	0.06	0.003
	Max	68.9	2.19	1.66	0.053
	Mean	17.95	0.78	0.43	0.019
	SD	11.45	0.43	0.28	0.010
Mg^{2+}	Min	0.06	0.005	0.01	0.000
	Max	7.94	0.585	0.72	0.053
	Mean	1.52	0.116	0.14	0.011
	SD	1.81	0.134	0.16	0.012
K^{+}	Min	0.02	0.001	0.02	0.001
	Max	0.57	0.006	0.57	0.006
	Mean	0.13	0.003	0.13	0.003
	SD	0.09	0.001	0.09	0.001
Na^{+}	Min	0.86	0.033	0.001	0.050
	Max	28.1	0.680	0.043	1.047
	Mean	9.43	0.254	0.015	0.390
	SD	6.83	0.155	0.010	0.239
Cl^{-}	Min	0.32	0.009	0.00	0.14
	Max	32.8	0.702	0.49	10.4
	Mean	7.11	0.155	0.11	2.32
	SD	5.34	0.108	0.05	1.61
F^{-}	Min	0.00	0.00	0.05	0.002
	Max	0.03	0.034	0.57	0.561
	Mean	0.01	0.001	0.21	0.018
	SD	0.01	0.004	0.13	0.071
NO_3^{-}	Min	0.17	0.002	0.10	0.001
	Max	6.17	0.052	3.85	0.033
	Mean	1.14	0.014	0.71	0.009
	SD	1.18	0.012	0.73	0.008
CO_3^{2-}	Min	0.89	0.024	0.025	0.001
	Max	8.92	0.249	0.248	0.007
	Mean	4.00	0.113	0.111	0.003
	SD	1.78	0.048	0.045	0.001
HCO_3^{2-}	Min	0.86	0.014	0.024	0.000
	Max	21.2	0.348	0.590	0.010
	Mean	7.92	0.102	0.220	0.003
	SD	5.05	0.056	0.140	0.002
SO_4^{2-}	Min	0.26	0.004	0.007	0.000
	Max	13.7	0.177	0.380	0.005
	Mean	2.67	0.048	0.074	0.001
	SD	2.23	0.035	0.061	0.001

Hazard quotient (HQ) indices

Table 7 also summarizes the HQ indices of selected major cations and anions in the study area through regular consumption of groundwater for various purposes in the study area. The mean HQ index values for Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, F^{-} and NO^{3-} for groundwater water during summer were 0.43, 0.14, 0.13, 0.11, 0.21 and 0.71 respectively. Similarly, for groundwater winter samples the mean HQ index values were 0.019, 0.011, 0.003, 2.32, 0.018 and 0.009. The HQ value for chloride indicates higher with 2.32 when compared to other parameters. Cl^- is one of the major inorganic anions in water and consumable water, the salty taste is delivered by the chloride ions. There is no known evidence that chlorides constitute any human health hazard and for this reason, chlorides are limited to 250 mg/L in supplies intended for public use (WHO 2014). Therefore, the order of distribution of cations and anions based on their mean concentration values during summer season is of the order $Cl^- > K^+ > Mg^{2+} > F^- > Ca^{2+}$ and NO^3 for groundwater and during winter seasons the order of distribution was $Cl^- > K^+ > NO^3 > Mg^{2+} > F^- > Ca^{2+}$.

Conclusions

This study reported the groundwater quality, toxicity and health risk in an industrial area by using various multivariate statistical and health risk methods for twenty physiochemical constituents of 120 groundwater samples collected during summer and winter seasons. The study area results demonstrated that both natural and anthropogenic processes were the two major factors for the chemical compositions of groundwater. The water quality results revealed that Ca–Na–Mg–HCO_3 type with dominant concentrations during both summer and winter seasons respectively contributing to the groundwater salinity. The multiple regression analysis for physicochemical constituents exhibited the highest correlation ($r > 8.0$) during summer and winter. Results from factor analysis indicated that Ca–Cl–CO_3–HCO_3–EC–TDS were dominating in factor 1 which were primarily from water–rock interaction like granite rock and slightly from anthropogenic inputs. Whereas, factor 2 is dominated by toxic heavy metals As–Cr–Cd–Ni–Pb–Zn combined during summer and winter seasons in groundwater from sources related to industrial waste, effluents release and human activities. The health risk hazard evaluation like CDI and HQ records exhibited that the groundwater is safe to drink given some water treatment systems are involved. Overall, the multivariate and risk assessment approach suggests goodness of these statistical techniques in the source apportionment of industrial waters and can be ranked in the order of mean cation values $K < Mg < Na < Ca$, anion concentrations arise in the order of $F < NO_3 < SO_4 < CO_3 < Cl < HCO_3$ and heavy metals occur in the order $Cd < As < Ni < Cu < Cr < Pb < Zn$.

Recommendations

The present study suggests that regular monitoring of the quality of groundwater should be undertaken temporally and spatially to identify the source of toxic pollutants and other inhibitory chemicals which affect the water around industries and design some remedial techniques to prevent the pollution caused by hazardous toxic elements in future.

Abbreviations

PCA: principal component analysis; HCA: hierarchical cluster analysis; CA: cluster analysis; FA: factor analysis; CDI: chronic daily intake; HQ: hazard quotient; KIDA: Katedan Industrial Development Area; ICP-MS: inductively coupled plasma mass spectrometry; GPS: global positioning system.

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Authors' contributions

In this manuscript AKK has contributed towards initiation of the idea, filed sampling, and interpretation of the data using multivariate statistical tools towards groundwater quality, contamination and health risk assessment. KRM has carried out filedwork and analysed physicochemical parameters and their interpretation. BD has assisted in carrying out filed sampling and sample preparation. All authors read and approved the final manuscript.

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