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Groundwater iron and manganese source apportionment in Chandrapur District, Central India

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Abstract

Grab sampling method was used to sample groundwater from 36 sampling locations from the Chandrapur district in three seasons i.e. winter, summer, and post-monsoon. The samples were analyzed for physiochemical parameters and heavy metals viz. iron and manganese. Data obtained from the study area was interpreted by using multivariate statistical analysis i.e. Principal component analysis, cluster analysis, correlation matrix and one way ANOVA to ascertain source apportionment of these two heavy metals. The results of the multivariate analysis revealed iron and manganese both were associated with the lithogenic source. Groundwater iron concentration was more as compared with manganese and at a number of sampling locations, it was above the stipulated standard of BIS (0.3 mg/L).

Keywords: Central India, Chandrapur, Cluster analysis, Correlation matrix, Heavy metal, Iron, Manganese, Source apportionment.

Introduction

Groundwater serves as a main source of drinking water and inhabitants depends upon it to carry out their day-to-day activities[1-3]. Of the world population >50% rely on groundwater for drinking purpose[4]. Groundwater is the only source of drinking water for number of rural and small communities[5]. Residing population in urban area is estimated to be >50%. About 50% mega-cities in developing world with population >10 million are depend upon groundwater[6]. Over one billion people lack access to clean safe water worldwide[7,8]. About 300 million rural inhabitants from sub-Saharan Africa have no access to safe water supplies. In absence of safe drinking water near dwellings, the livelihood and health of these inhabitants is severely affected[9,10].

Groundwater exploitation is generally considered as the only realistic option for meeting dispersed rural water demand[10]. This is due to easy accessibility of groundwater anywhere, with less capital and maintenance investment, less prone to pollution and further seasonal variation and pristine quality[7,11]. Due to increasing demand and withdrawal of groundwater, land use change, pollution and climate change its quality is under intense pressure[12,13].

In India, 200 million people do not have access to clean drinking water. At present, only 85% of the urban and 79% of the rural population has access to safe drinking water. India is facing a water quality crisis. Toxic organic and inorganic pollutants already contaminate a growing number of groundwater reserves. Water being an universal solvent has a tendency to dissolve everything that comes to its way thus increasing its chances of contamination and alter its quality[6].

Universal access to clean and safe drinking water is considered as a basic human right by United Nations. The stress on water resources is from multiple sources and the impact can take diverse forms[14]. Anthropogenic activities released chemicals and heavy metals into groundwater have emerged as a global concern[15]. The contamination of water resources has important repercussions for the environment and human health[16,17]. In the world about 2.3 billion individual suffer from water related diseases[18,19]. Excessive ingestion of drinking water contaminated with heavy metals may have carcinogenic effects on human health[17].

Iron is abundantly available in the Earth's crust and in natural aquatic environment it rangers from 0.5 to 50 mg/L. It is an essential element in human nutrition. Manganese usually occur with iron is also abundantly available in Earth's crust. It is essential for human and animal and is available in many food sources. Manganese is available in natural aquatic environment. It has been reported that extended exposure to elevated levels of manganese may have adverse neurological effects[20].

Drinking water quality in mafic and ultramafic rocks in northern Pakistan reported trace metals such as iron, manganese, nickel, chromium, and cobalt[21]. Iron in groundwater ranged from 134 to 5200 µg/L (mean ~1422 µg/L)[22]. Oyem *et al.*, (2015) reported higher iron content in groundwater of Boji-Boji Agbor area (27%) and highest manganese (31%) in Boji-Boji Owa area of Nigeria[23]. Melegy *et al.*, (2014) reported about 50% of the studied groundwater and surface water samples (n=42) contain a high concentration of iron above drinking water guidelines of WHO (2011)[24]. As reported by Khan *et al.*, (2013) concentration of iron exceeded its permissible limit from isolated locations of Charsadda district, Pakistan[25]. Ingestion of high level of iron causes number of diseases[26]. Utom *et al*., (2013) reported up to 42% of analyzed groundwater samples iron concentration was beyond the Nigerian Industrial Standard; whereas, manganese concentration was in the range of 0.03-2.6 mg/L and 25% sampling locations reported the concentration above the permissible limit[27].

According to Ocheri (2010), variation in iron concentrations may be attributed to number of activities[28]. Ibe *et al*., reported high groundwater iron concentration and may be due to leaching of iron from iron scraps at the landfill site and from galvanized iron pipes in hand pumps equipped wells[29]. The plausible source for the high iron concentration may be attributed to leaching from ferruginized sandstone and lateritic overburden. Iron concentration in groundwater may increase or decrease with the increasing depth of aquifers[30]. Hatva (1989) reported iron and manganese contents in groundwater of Finland varied widely depending on aquifer structure, flow pattern and oxygen balance[31]. Multivariate analysis showed that iron was associated with the lithogenic source[32]. Alam and Umar reported relatively high concentrations for iron and manganese in few samples[33]. The groundwater iron source was associated with weathering followed by dissolution of iron-bearing ores. The origin of groundwater iron was attributed to the geogenic source[34]. Iron is released into water due to weathering processes and corrosion products [35]. Elevated manganese concentrations were associated with iron ores as well as lateritic mining[36]. According to Giri *et al*. iron and manganese exceeded the IS 10500 standards in many locations. The elevated levels of Fe and Mn were due to the natural occurrence of mineralization and background rock geochemistry. Summer season reported the elevated concentration of contaminants due to the decrease in the groundwater table[37]. Chakrabarty and Sarma, attributed the possible source of origin of manganese to geogenic in nature[38]. Bhuyan reported groundwater was contaminated with iron which was attributed to geogenic in origin[39]. Srinivasa Rao reported iron was found to correlate considerably better with manganese in fluvial and coastal alluvium zones[40].

From the review of the related literature and researches, it was observed that selected studies have been carried out pertaining to groundwater heavy metals from the Chandrapur district. However, no significant emphasis was stressed upon groundwater iron and manganese and their source apportionment in particular. This is the identified gap in the research and new knowledge in this regard needs to be added to this subject domain. Hence, this study was proposed to carry out.

Methodology

Study area: Chandrapur district (19°25’ N to 20°45’ N and 78°50’ E to 80°10’ E) is situated in the Vidarbha region of Maharashtra state of central India (Figure-1). The district is the easternmost district of the state. The district covers an area of 11,364 sq km with elevation ranging from 106 m to 589 m asl, the south-west part having a high level and south-east part with low level. The district comprises of 15 administrative blocks and is surrounded by other districts such as Nagpur (north of northwest), Wardha (northwest), Yeotmal (west), Adilabad (south), Gadchiroli (east) and Bhandara (north). The district is bestowed with natural bounty in the form of dense forest and wildlife on one hand and on other minerals such as coal, limestone, iron, copper etc. Due to abundant presence of natural resources and minerals, the district has witnessed sprawling coal mines, cement industries, pulp, and paper industry and a number of thermal power plants and at the same time Tadoba Andhari Tiger Reserve (TATR) which has one of the largest numbers of tigers in central India.

Climate and rainfall: The climate of the district is characterized by wide climatic conditions ranging from hot summer (May, temperature up to 47°C) to cold winter (December, temperature up to 7°C) and general dryness throughout the year. The district has tropical hot climate. The humidity was observed as 70% during monsoon and 20% in summer. The rainy season (June-September) had reported rainfall from south-west monsoon with an annual rainfall ranging from 1200-1450 mm with an annual number of rainy days as 60 to 65. The rainfall is asymmetrically distributed in the district. The Worora tehsil receives comparatively minimum rainfall which gradually increases and reaches to a maximum around Bramhapuri tehsil[41].

Geomorphology: The geomorphology of the district is divided into plain region and hilly region. The plain region is widely spread and flat is along the Wardha River. Flat terrain is observed in southern part with hills[41].

Hydrogeology: The groundwater in Chandrapur district exists under confined/semi-confined and unconfined conditions. The depth of unconfined aquifer was up to 20 m bgl and can be tapped by dug well. Groundwater declining trend at a rate of >20 cm per year (Pre-monsoon 1995-2004) was recorded in the district (MPCB, 2006)[42]. The groundwater flow in the district is observed towards Wardha River and its tributaries thus making the affluent nature of the river[43].

Geology: Chandrapur district is a part of Gondwana sedimentary basin. The brief description of these stratigraphic units includes:

Archean formations: Granites are holocrystalline rocks typically composed of quartz, feldspar and mica or hornblende and are of very varying grain; in this district, they are also associated with diorites and other holocrystalline basic rocks. Gneisses consist of gneiss proper-a foliated crystalline basic rock having much the same constituents as granite-with schists of hornblende, mica, and quartz and with much vein quartz. Dharwars, as they occur in the district, are highly altered shales (argillites) with some quartzites, sometimes ferruginous and with some micaceous schists[44].

Purana formations: Resting unconformably on the gneisses occur the Vindhyan consisting mostly of sandstones, quartzitic sandstones, and quartzites with some shales and limestones. The Vindhyan of the district belongs to the Lower Vindhyan series[44].

Aryan formations: The rock of the Talchir group, the lowermost member of the Gondwana series, are generally fine buff sandstones, greenish-gray silty shales and sandstones, underlaid by a bed containing boulders polished and striated, this striation or scratching being supposed to be due to glacial action. The Barakar group is notable as containing all the workable beds of coal. Beginning from the top the arrangement of layers is 1) coal, 2) sandstone and shales, 3) carbonaceous beds and 4) sandstones and shales. The Kamthi group is found resting unconformably on the Barakars. The rock composing it are 1) grit, more or less compact, 2) sandstones, coarse or fine-grained, with red blotchy streaks, with some conglomerate and 3) sandstones, argillaceous and ferruginous. Clays, usually red and green and shales of various colours occur intercalated among the sandstones. The rocks constituting the Kota- Maleri group are mainly red and green clays and argillaceous sandstones, the basal sandstones containing green clay-galls; limestone beds are found in association with the clays. The Deccan Trap series is composed of volcanic lavas and has been classified into upper, middle and lower traps; beneath it lie basal sedimentary beds, known as Lameta or Infratrappean, consisting of sandstones, sometimes calcareous, with limestone's, which are generally cherty and impure and some clays. Intercalated among the lava-flows occur volcanic ash beds and also some sedimentary beds; these latter are known as inter-trappean beds. The only traps found in the district belong to Lower Trap group. Laterites are next in succession to the trappean rocks and later still are the various deposits which include all the soils of the present area. In the river valleys, ossiferous gravels often cemented into a conglomerate of tolerable hardness are of frequent occurrence[44].

Groundwater sampling and analysis: Thirty-six groundwater sampling locations comprising of hand pumps and dug wells from the Chandrapur district were identified in Figure-2 and Table-1. Stratified sampling was carried out for groundwater sampling. Of these sampling locations, 34 (94.44%) were from hand pumps and two (5.55%) from dug wells. The sampling locations were selected such that maximum study area to be covered. Furthermore, these sampling locations were selected from rural areas where inhabitants were mostly dependent upon groundwater as a source of potable water and to carry out other domestic activities. Grab sampling method was adopted to carry out groundwater sampling.

For collecting groundwater samples for analysis two different capacities of polyethylene containers were selected. For analysis of general parameters (physicochemical), a narrow mouth polyethylene container of 1000 mL capacity (Poly lab, India) was selected; whereas, for heavy metals analysis a narrow mouth 100 mL capacity polyethylene container (Poly lab, India) was used. These both containers were thoroughly washed first with detergent than with distilled water followed by conc. HNO_3 (16 *N*, Merck) further by repeated washing with distilled water in the laboratory. Heavy metals samples were preserved by adding conc. HNO_3, 2 mL per 100 mL at the time of sampling. All reagents used while carrying out physicochemical analysis was of AR grade (Merck) and glassware was of borosilicate make. Double distilled water was used for the preparation of reagents. All reagents were prepared as stated in APHA (2005)[45]. Total heavy metals concentrations were determined after acid digestion with conc. HNO_3[46]. Heavy metals analysis was carried out by using ICP-OES (ICP-OES, Perkin Elmer, Germany, Dv 7000).

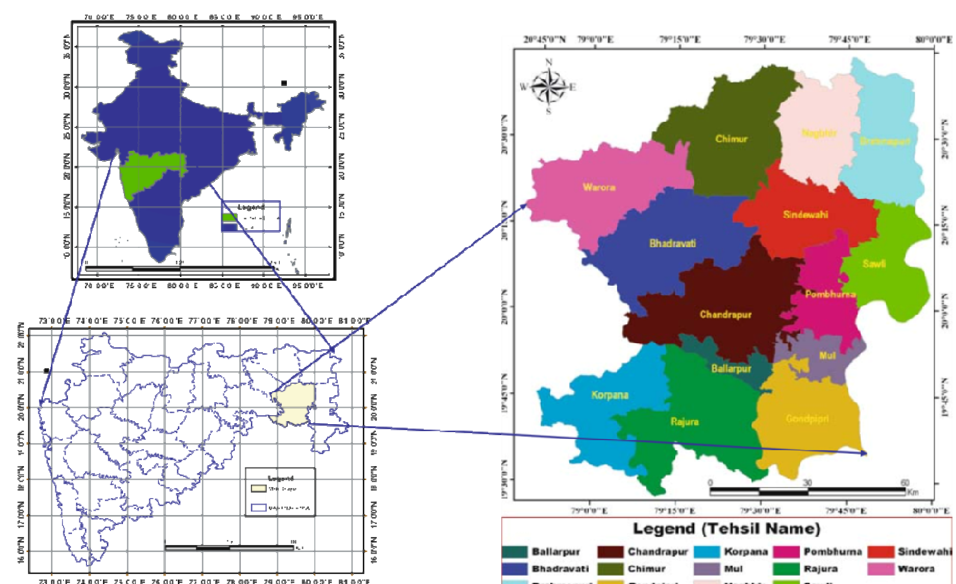

Figure-1: Chandrapur district with administrative blocks[43].

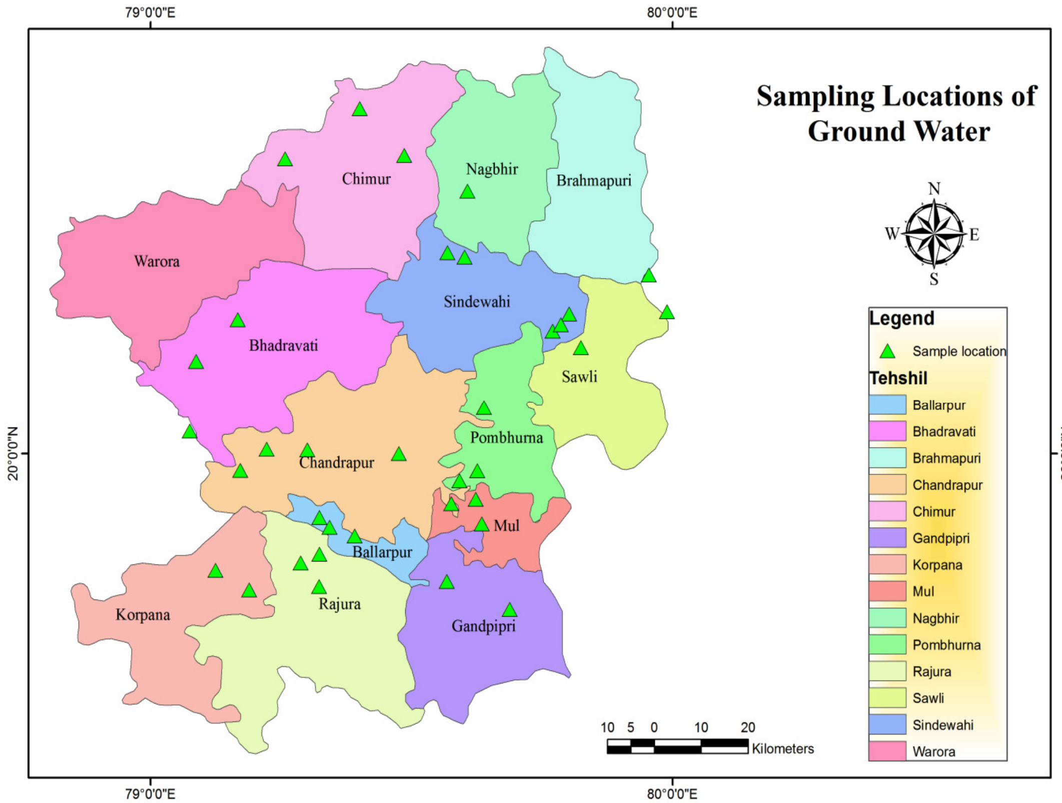

Figure-2: Groundwater sampling locations from the study area.

Statistical analysis: Different statistical analyses were carried out for the interpretation of data i.e. Principal component analysis, cluster analysis and correlation analysis[47]. The correlation coefficient in the form of a matrix was calculated[48]. One way ANOVA was used to estimate the measurement uncertainty[49].

Results and discussion

Groundwater sampling locations were located at different altitudes in the range of 152-287 m asl, year of installation from 1 to 60 years (age), depth of 20-300 feet below ground level (ft bgl) and iron and manganese concentrations variation in different seasons (Table-1). Groundwater samples were analysed for different physicochemical parameters: pH, total dissolved solids (TDS) (mg/L), chlorides (mg/L), iron (total) (mg/L) and manganese (total) (mg/L). These parameters average values were calculated from three seasons (winter, summer, and post-monsoon).

The range was 5.8-7.4 (pH), 190.0-3496.66 (TDS), 8.170-886.98 (chlorides), 0.081-18.213 (iron) and 0.003-0.779 (manganese). The average value of total heavy metal content in the groundwater sample was in the order of iron>manganese. Maximum iron and manganese concentration from the samples was above the BIS permissible limit for respective metal (IS 10500:2012) (Table-2).

Figures-3, 4, 5 and 6 depict thematic maps for groundwater iron concentrations and Figures-7, 8, 9 and 10 depict thematic maps for groundwater manganese concentrations for winter, summer, post-monsoon, and average concentration respectively. Minimum iron concentration in winter, summer and post-monsoon was BDL, 0.164 mg/L (Sagra, DW) and 0.055 mg/L (Gunjewahi, DW) respectively; whereas, maximum 47.100 mg/L (Ballarpur, HP), 3.825 mg/L (Ballarpur, HP) and 4.022 mg/L (Visapur, HP) respectively. Maximum average iron concentration was in Ballarpur (HP) 18.213 mg/L and minimum in Gunjewahi (DW) 0.081 mg/L. The iron concentration in Ballarpur was 47.100 mg/L in winter, 3.825 mg/L in summer and 3.714 mg/L in post-monsoon. Seasonal variation in groundwater iron concentration was recorded. Maximum iron concentration was found to be elevated and above the permissible limit of 0.3 mg/L of the Indian Standard (2012) and aesthetic limit of WHO (2006) for iron. Groundwater manganese concentration in winter was in the range of BDL to 1.853 mg/L (Naleshwar, HP) in summer 0.003 mg/L (Morwa, HP) to 0.474 mg/L (Ganpur, HP), whereas in case of post-monsoon it was in the range of 0.002 mg/L (Ganpur, HP) to 0.761 mg/L (Bhisi, HP). Average manganese concentration was in the range of 0.003 mg/L (Morwa, HP) to 0.779 mg/L (Naleshwar, HP). Seasonal variation in groundwater manganese concentration was recorded. Maximum manganese concentration was found to be elevated and above the permissible limit of 0.1 mg/L of the Indian Standard (2012).

Table-1: Groundwater sampling locations and characteristics

Sampling location	Age (Years)	Depth (ft bgl)	Average pH	Average TDS	Average Cl^-	Average Fe conc.	Average Mn conc.
Sonegaon (HP)	3	100	7.05	596.67	11.94	0.110	0.008
Telwasa (HP)	3	100	6.89	840.00	53.73	0.251	0.004
Belora (HP)	10	100	7.27	646.67	38.68	0.109	0.047
Sagra (DW)	57	50	7.25	1116.67	120.55	0.081	0.007
Pethbhansouli (HP)	3	100	7.05	833.33	91.86	5.090	0.412
Bhisi (HP)	1	150	6.8	1200.00	162.77	0.647	0.376
Pimpalgaon (HP)	25	250	7.02	1913.33	315.41	0.873	0.027
Mowada (HP)	10	180	7.11	783.33	65.80	0.173	0.003
Dongargaon (HP)	30	200	6.8	1440.00	223.44	0.871	0.372
Lohara (HP)	12	60	5.81	190.00	15.25	1.457	0.011
Chichpalli (HP)	12	70	6.93	3496.67	886.99	0.124	0.144
Dabgaon (T.) (HP)	3	300	6.87	1606.67	255.54	2.236	0.222
Naleshwar (HP)	12	140	6.57	1296.67	329.30	0.693	0.779
Karwan (HP)	8	150	7.33	673.33	58.68	0.128	0.053
Chikmara (HP)	25	100	6.98	1166.67	154.97	0.410	0.022
Pathri (HP)	20	100	6.73	586.67	79.44	0.190	0.057
Gunjewahi (DW)	60	35	7.44	400.00	17.41	0.081	0.003
Mangali Chak (HP)	25	200	7.04	466.67	19.66	0.176	0.003
Govindpur (HP)	25	150	6.93	1640.00	357.68	0.195	0.031
Ratnapur (HP)	10	100	6.87	996.67	158.05	1.441	0.113
Antargaon (HP)	15	200	7.49	616.67	8.17	0.164	0.003
Visapur (HP)	9	100	6.31	580.00	75.74	5.766	0.131
Ballarpur (HP)	5	60	6.12	560.00	63.70	18.213	0.045
Sasti (HP)	10	180	6.83	1980.00	269.49	2.270	0.088
Gowari (HP)	6	120	7.08	1006.67	102.43	0.308	0.003
Arvi (HP)	23	100	6.8	1003.33	97.69	0.524	0.005
Awarpur (HP)	2	200	7.13	1586.67	171.57	0.230	0.034
Lakhmapur (HP)	8	200	6.88	593.33	11.45	1.280	0.006
Kem (T.) (HP)	8	150	7.11	400.00	8.53	1.779	0.057
Ganpur (HP)	25	160	6.82	2720.00	435.26	0.601	0.004
Gondpipari (HP)	20	100	6.8	1446.67	230.97	1.562	0.287
Pombhurna (HP)	20	100	6.96	1246.67	177.45	0.310	0.008
Jam Tukum (HP)	20	250	6.9	1910.00	365.94	0.257	0.060
Dongar Haldi (HP)	6	120	7.01	1980.00	349.78	0.709	0.091
Durgapur (HP)	4	20	6.95	1866.00	219.72	0.256	0.286
Morwa (HP)	15	100	7.04	1180.00	116.27	0.251	0.003

Altitude in meters above sea level; Water source HP - Hand Pump, DW - Dug Well; Age - Age of the hand pump or dug well; Depth - in feet below ground level (ft bgl).

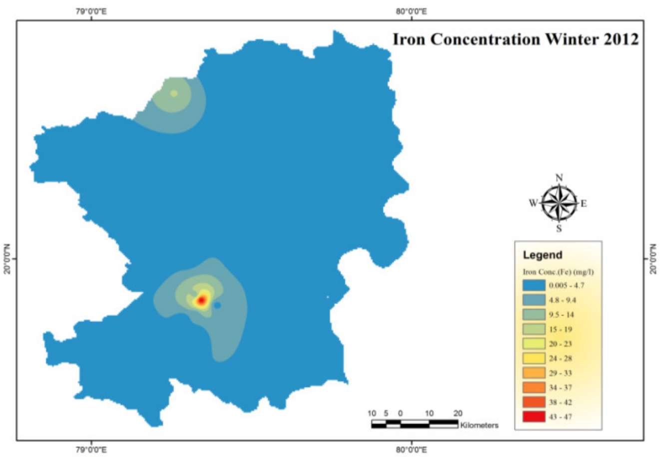

Figure-3: Thematic map of iron concentrations (Winter)

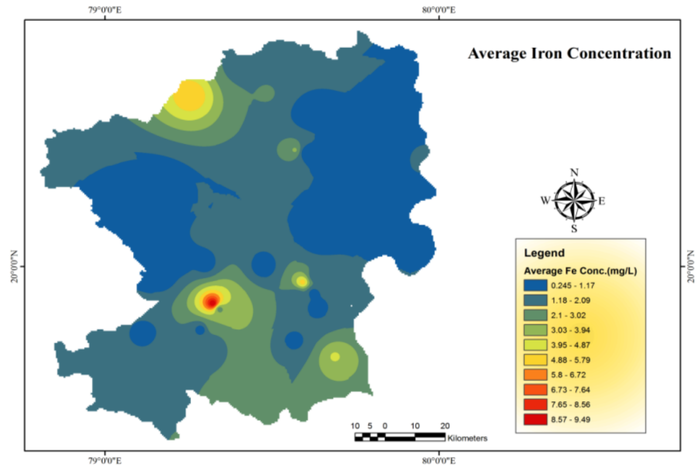

Figure-6: Thematic map of average iron concentrations.

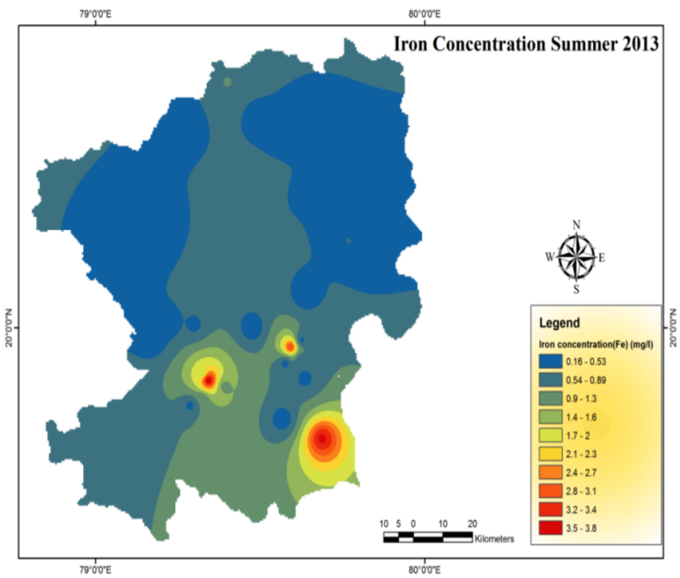

Figure-4: Thematic map of iron concentrations (Summer)

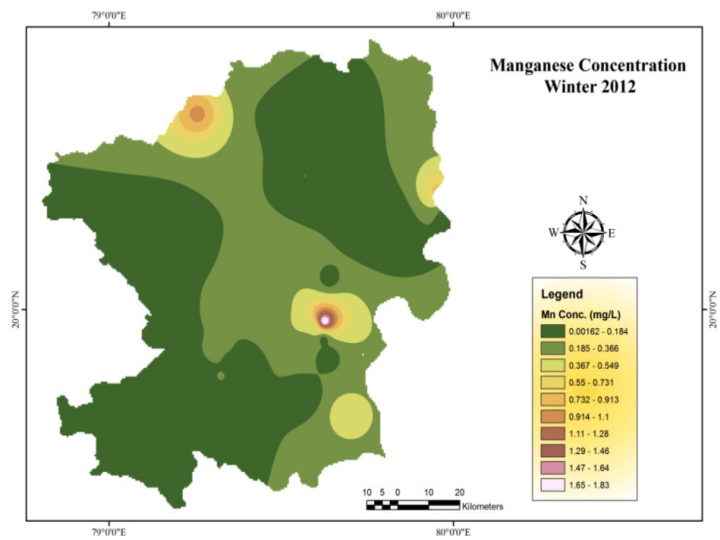

Figure-7: Thematic map of manganese concentrations (Winter).

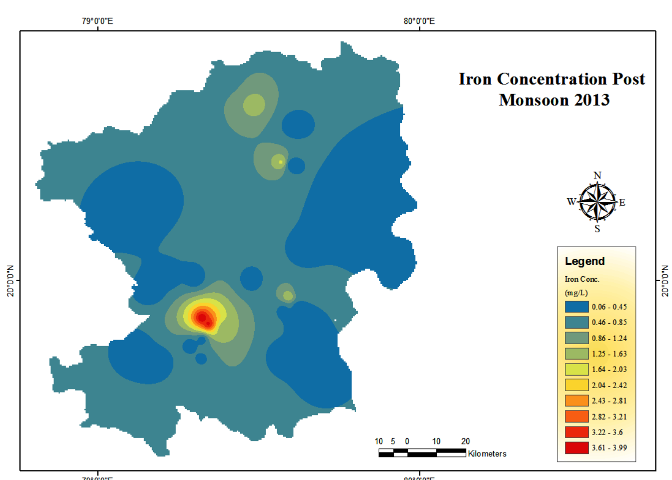

Figure-5: Thematic map of iron concentrations (Post-monsoon)

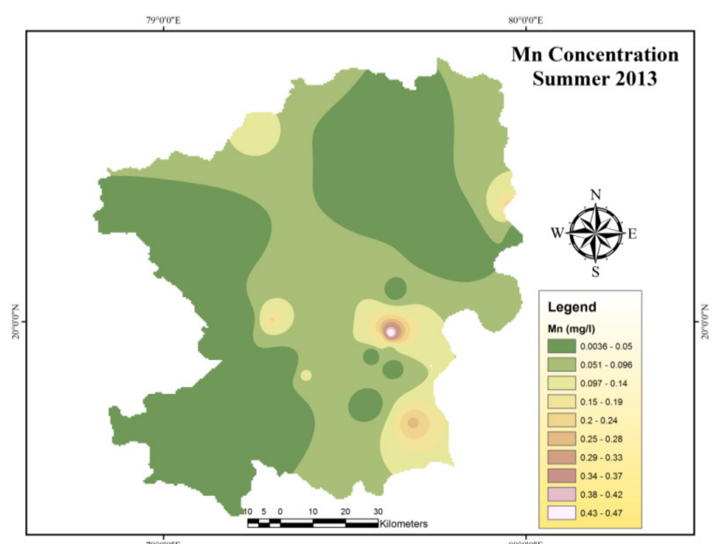

Figure-8: Thematic map of manganese concentrations (Summer)

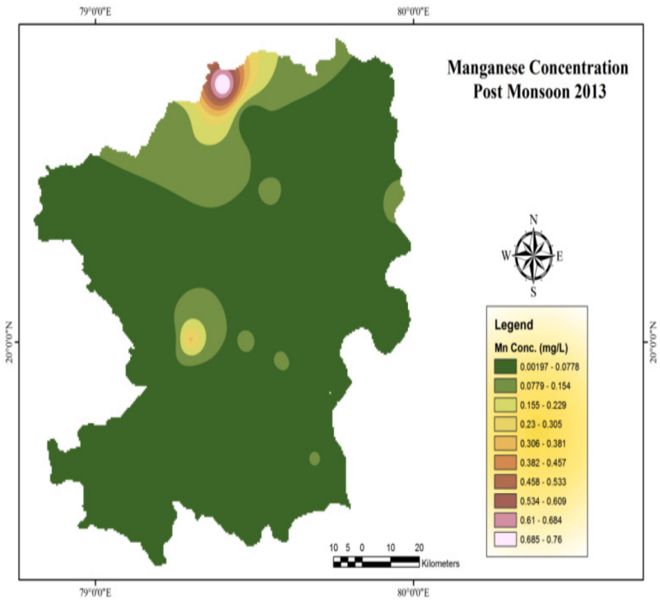

Figure-9: Thematic map of manganese concentrations (Post-monsoon)

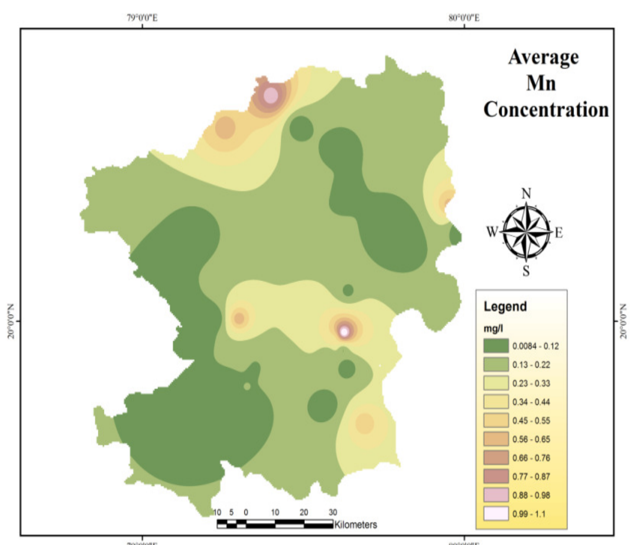

Figure-10: Thematic map of average manganese concentrations.

Higher iron concentrations from hand pump were in agreement with results reported by[43,50]. Hand pumps owing to their close proximity to ores and minerals present in the Earth crust and water being a universal solvent tends to dissolve these ores and minerals and resulted into such an elevated iron concentration than dug wells. Utom *et al*., (2013) reported a minimum manganese concentration of 0.03 mg/L and maximum as 2.6 mg/L[27]. Groundwater manganese concentration reported by Purushotham *et al*., (2013) was in the range of 2.3 to 4340 µg/L with an average of 2171 µg/L[51]. Alam and Umar (2013) reported manganese concentration range from 0.024 to 0.56 mg/L[33]. Maximum manganese concentration (0.56 mg/L) in comparison with results of the existing study indicates that it is comparable with summer (0.474 mg/L). Maximum groundwater manganese concentration as reported by Agca *et al*., (2014) was 1.026 mg/L[52]; Cobbina *et al*., (2012) was 1.05 mg/L[53]; Hasan and Ali (2010) was 9.98 mg/L[54]; Homoncik *et al*., (2010) was 1.9 mg/L[55]; Melegy *et al*., (2014) was 3.0 mg/L[24] and Nawankwoala *et al*., (2011) was 2.34 mg/L[56] which again highlights that in natural aquatic environment elevated manganese concentrations can be obtained.

Principal Component Analysis: Principal Component Analysis (PCA) results for winter (Table-3) shows that iron and manganese had rotated component matrix of 0.771 and 0.481 respectively, which was more than pH, TDS, and Cl^-. This suggests that the distribution of iron and manganese had a lithogenic origin and therefore these two heavy metals were included in the second principal component.

In the case of summer (Table-4), iron and manganese had rotated component matrix of 0.841 and 0.502 respectively which was more than pH, TDS, and Cl^-. Factor loading plot for the summer is depicted in Figure-12 which shows that iron and manganese at the positive axis of the plot and in comparatively close proximity with each other (as compared with winter) indicates that they were originated from a single source–natural lithogenic origin. As compared with the winter (Figure-11), iron and manganese were in close proximity to each other in the summer. The plausible reason which can be assigned for this observation was prevailing environmental conditions in the aquatic environment. Due to a decrease in groundwater level in the summer, reduced (or no) dissolved oxygen and reduction in weathering and dissolution of minerals and ores present in the Earth crust can be assigned as contributing factors for such observations. In winter due to dilution of heavy metals concentration which got accumulated in the summer had resulted in observation as depicted in Figure-11. Although iron and manganese were in similar axis and on the positive side of the plot they were away from each other as compared with the winter.

In the case of the post-monsoon (Table-5), the component matrix and rotated component matrix which was divided into PC1 and PC2 as an anthropogenic and natural source of origin shows that iron and manganese were found in amounts greater than 0.7 and 0.3 in the component matrix and in case of rotated component matrix they were -0.860 and -0.221 (Figure-13). It may be stated that the post-monsoon had a negative impact on the concentration of these two heavy metals into consideration.

Rotated component matrix for winter and summer shows that higher observations in PC2 as that of PC1 and further they were strongly correlated with iron at >0.7 and manganese at >0.4. This indicates, during these two seasons the source of heavy metals into groundwater was geogenic in origin. In the case of the post-monsoon after rotated component matrix, iron and manganese concentration reported negative observations, although negative, iron had a strong correlation (-0.860).

Table-2: Basic parameters for collected water samples.

Parameter	Min.	Max.	Average	Std. Dev.	BIS
pH	5.8	7.4	6.9	0.3	6.5-8.5
TDS	190.00	3496.66	1182.38	699.24	500
Cl-	8.17	886.98	170.03	172.33	250
Fe	0.081	18.213	1.384	3.153	0.3
Mn	0.003	0.779	0.106	0.165	0.1

Min.- Minimum, Max.- Maximum, Std. Dev.- Standard Deviation. BIS - Bureau of Indian Standard (IS 10500:2012) permissible limit

Table-3: Principal Component Analysis (Total variance) (Winter)

Component	Initial Eigen value			Groundwater characteristic	Component matrix[a]		Rotated component matrix	
	Total	%Variance	Cumulative %		PC1	PC2	PC1	PC2
1	2.432	48.637	48.637	Fe	-.248	.776	-.263	.771
2	1.264	25.271	73.908	Mn	.437	.473	.428	.481
3	.683	13.662	87.570	pH	-.108	-.831	-.091	-.833
4	.578	11.553	99.123	TDS	.947	-.117	.949	-.098
5	.044	.877	100.000	Cl^-	.974	.007	.974	.026

Extraction method: Principal Component Analysis. Rotation method: Varimax with Kaiser Normalisation. [a]Rotation converged in 3 iterations.

Table-4: Principal Component Analysis (Total variance) (Summer)

Component	Initial Eigen value			Groundwater characteristics	Component matrix[a]		Rotated component matrix	
	Total	%Variance	Cumulative %		PC1	PC2	PC1	PC2
1	2.050	40.997	40.997	Fe	.172	-.829	-.095	.841
2	1.537	30.749	71.746	Mn	.411	-.393	.268	.502
3	.851	17.011	88.757	pH	-.256	.746	-.011	-.788
4	.522	10.440	99.196	TDS	.934	.297	.980	.009
5	.040	.804	100.000	Cl^-	.956	.227	.979	.082

Extraction method: Principal Component Analysis. Rotation method: Varimax with Kaiser Normalisation. [a]Rotation converged in 3 iterations.

Table-5: Principal Component Analysis (Total variance) (Post-monsoon)

Component	Initial Eigen value			Groundwater characteristics	Component matrix[a]		Rotated component matrix	
	Total	%Variance	Cumulative %		PC1	PC2	PC1	PC2
1	2.103	42.057	42.057	Fe	-.497	.709	-.102	-.860
2	1.429	28.588	70.645	Mn	.117	.313	.251	-.221
3	.962	19.233	89.878	pH	.444	-.751	.036	.872
4	.454	9.075	98.953	TDS	.931	.308	.966	.169
5	.052	1.047	100.000	Cl^-	.882	.411	.972	.055

Extraction method: Principal Component Analysis. Rotation method: Varimax with Kaiser Normalisation. [a] Rotation converged in 3 iterations.

The PCA results suggest that two factors contribute to groundwater contamination and iron contribution was more than that of manganese these findings is in accordance with the observations obtained by Purushotham *et al*., (2013) which states that iron contribution was more than manganese[51]. PCA carried out by Dwivedi and Vankar (2014) showed iron and manganese had lithogenic sources, similar conclusions are also drawn from the observations[32]. These findings are also in accordance with results obtained by Mico *et al*., (2006) which stated that iron and manganese appeared to be associated with parent rocks[57].

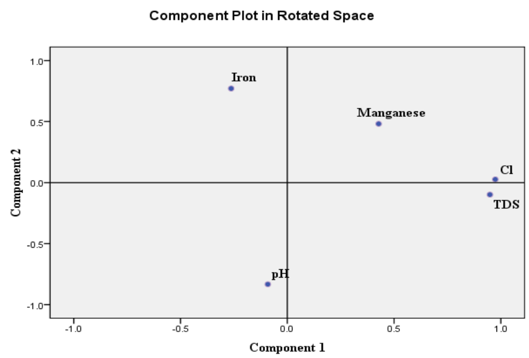

Figure-11: Plot of factor loading (Winter).

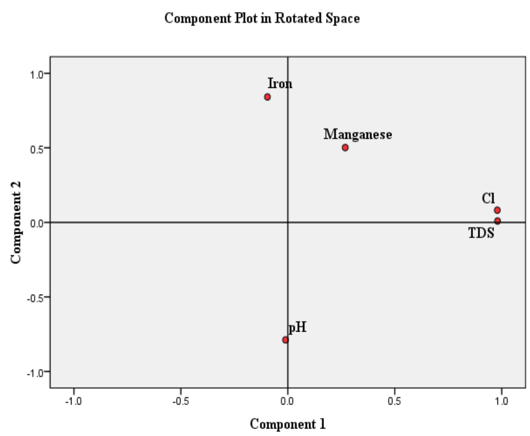

Figure-12: Plot of factor loading (Summer).

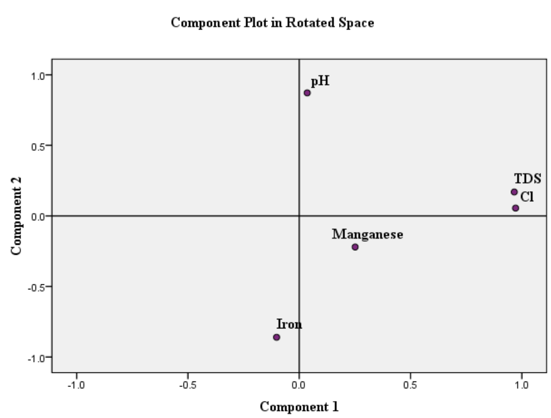

Figure-13: Plot of factor loading (Post-monsoon)

Cluster analysis

Iron: Cluster analysis results are shown in Figure-14 for groundwater iron concentrations in winter revealed three major clusters: 1) Ballarpur, 2) Pethbhansouli and Visapur and 3) other 26 sampling locations. Those sampling locations (n=7, 19.44%) where groundwater iron concentration was below detection limit (BDL) were not included in cluster analysis. From these three clusters, it can be suggested that 26 sampling locations which formed a major cluster had comparable groundwater iron concentrations (0.006-5.714 mg/L); whereas, Pethbhansouli (HP) and Visapur (HP) had formed another cluster with iron concentrations of 14.313 mg/L and 11.536 mg/L respectively. Ballarpur (HP) with 47.100 mg/L had elevated groundwater iron concentration formed another cluster. The cluster analysis suggested that groundwater iron was from geogenic in origin.

In the case of summer (Figure-15) groundwater iron is clustered into three major clusters: 1) Ballarpur, Gondpipari, and Dabgaon (Tukum), 2) Visapur and 3) other 32 sampling locations. Out of these three clusters, Ballarpur, Gondpipari, and Dabgaon (Tukum) and Visapur were closest in terms of groundwater iron concentrations. The remaining major group had comparable iron concentrations. All other sampling locations were grouped into this cluster. From this dendrogram, the major cluster of 32 sampling locations suggested that iron had originated from one source which can be assigned as geogenic in origin.

Similarly, cluster analysis for the post-monsoon (Figure-16) resulted in a dendrogram identifying close groundwater iron concentration groups. These three groups were: 1) Ballarpur and Visapur, 2) Dabgaon (Tukum), Ratnapur, Pimpalgaon and Kem (Tukum) and 3) remaining 30 sampling locations. From this third major cluster which showed groundwater iron concentrations were comparable. On the other hand, the second major cluster had comparable groundwater iron concentrations in the range of 1.2 to 1.7 mg/L. Visapur and Ballarpur cluster had near similar groundwater iron concentrations (4.022 mg/L and 3.714 mg/L, respectively). The close association of cluster 1 and cluster 2 was due to comparable groundwater iron concentrations. From the dendrogram which revealed a major cluster of 30 sampling locations indicated that groundwater iron concentration was from geogenic in origin.

Manganese: Cluster analysis for groundwater manganese concentrations in winter (Figure-17) indicates four major clusters: 1) Naleshwar, 2) Gondpipari, 3) Pethbhansouli and Dongargaon and 4) other 24 sampling locations. In this dendrogram 28 sampling locations were presented, other eight sampling locations due to ‘BDL’ were not presented. Sub-cluster included Pethbhansouli, Dongargaon, and Gondpipari. Clusters 1 and 2 had comparable results for groundwater manganese concentrations due to their closeness in the dendrogram. The major cluster of 24 sampling locations indicated groundwater manganese was from geogenic in origin.

In summer (Figure-18) revealed four major clusters: 1) Naleshwar, 2) Dongargaon, Durgapur, and Gondpipari, 3) Pethbhansouli, Dabgaon (Tukum), Chichpalli, Jam Tukum, Bhisi, Kem (Tukum) and 4) other 26 sampling locations. Clusters 3 and 4 due to the similarity in groundwater manganese concentrations had close proximity to each other. Cluster 1 which includes Naleshwar had highest groundwater manganese concentration (0.474 mg/L). From the dendrogram maximum sampling locations (n=26, 72.22%) had groundwater manganese concentration comparable with each other revealed that the manganese was from geogenic in origin.

Figure-19 indicates groundwater manganese for post-monsoon. The dendrogram indicates three clusters: 1) Bhisi, 2) Durgapur and 3) other 34 sampling locations. Bhisi (HP) had maximum (0.761 mg/L) groundwater manganese concentration, Durgapur (HP) with 0.312 mg/L and other 34 sampling locations had comparable concentrations. Clusters 1 and 2 were most similar in terms of groundwater manganese concentrations. From the third cluster, which forms the major cluster, shows that groundwater manganese was from geogenic in origin.

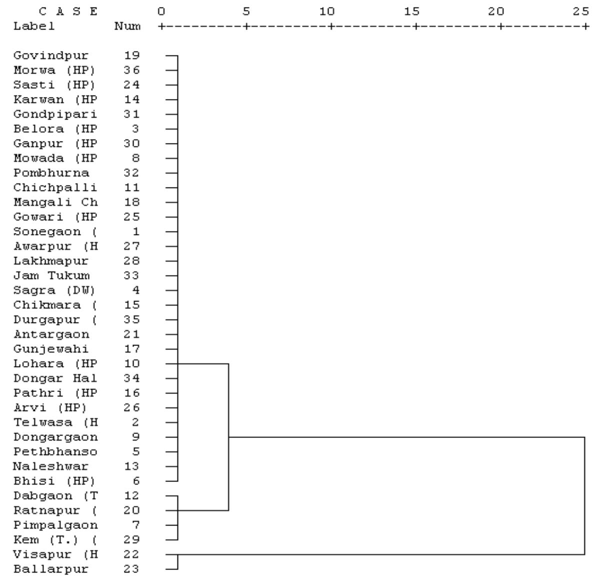

Figure-16: Cluster analysis of iron (Post-monsoon).

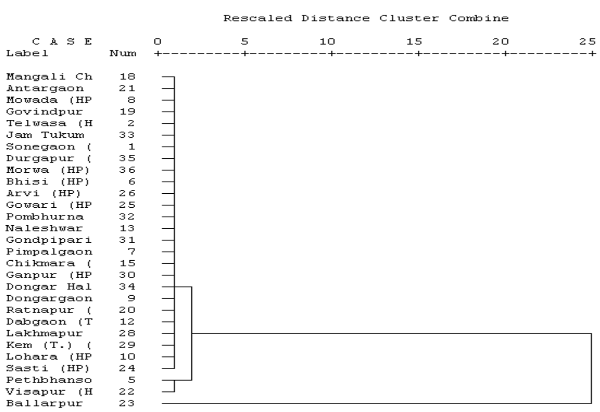

Figure-14: Cluster analysis of iron (Winter).

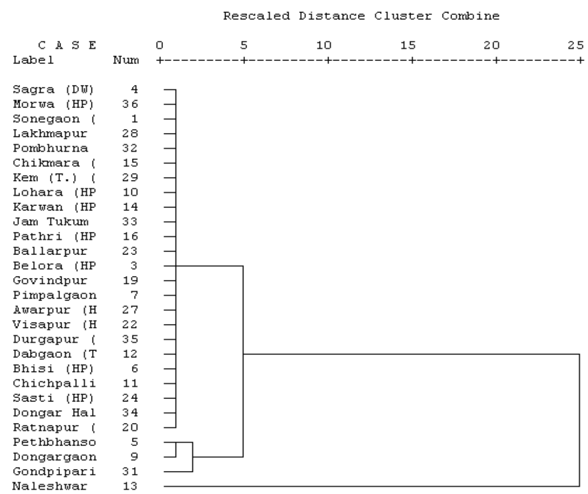

Figure-17: Cluster analysis of manganese (Winter).

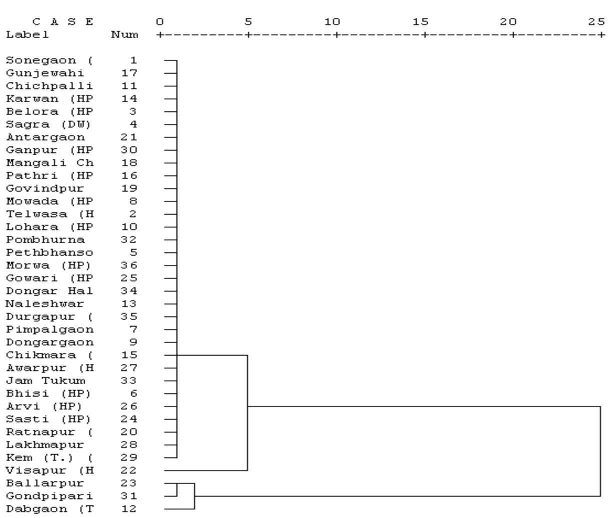

Figure-15: Cluster analysis of iron (Summer)

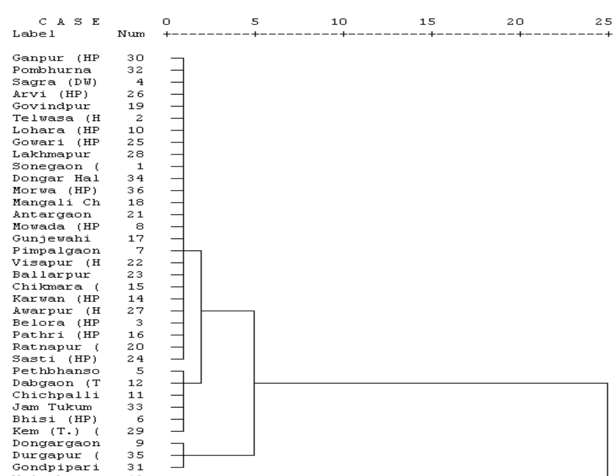

Figure-18: Cluster analysis of manganese (Summer)

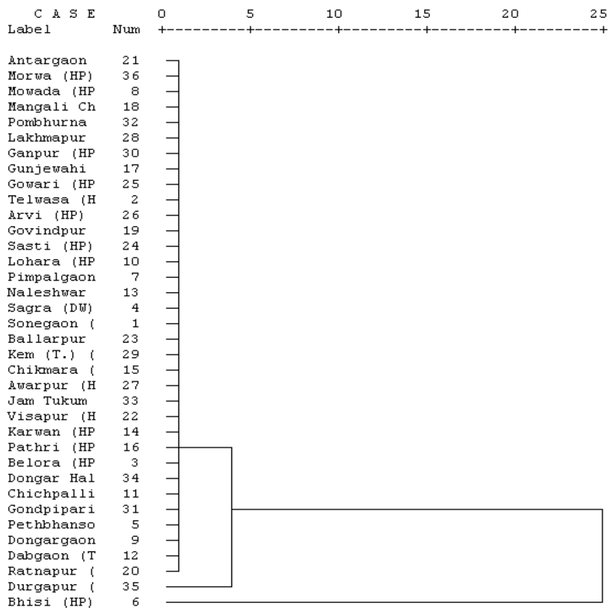

Figure-19: Cluster analysis of manganese (Post-monsoon).

Correlation matrix: Correlation matrix for iron, manganese, pH, TDS, and Cl^- with significant (1-tailed) in winter, summer, and post-monsoon are presented in Tables-6, 7 and 8 respectively. In winter (Table-6) correlation matrix for these selected five groundwater characteristics shows that iron and manganese had a correlation at a significant level of 0.312 (1-tailed), manganese and TDS with 0.145, pH and TDS with 0.474 and pH and Cl^- 0.265 at 1-tailed. The observations for significant (1-tailed) for the summer (Table-7) among different variables showed that iron had a significant relation (1-tailed) with TDS and chloride at 0.434 and 0.477 respectively. In the case of manganese with TDS and chloride, it was found to be 0.163 and 0.116 respectively significant. Observations for post-monsoon (Table-8) revealed that manganese with iron (0.408), pH (0.380), TDS (0.259) and Cl^- (0.327).

One way ANOVA: The test statistics for groundwater iron (Tables-9 and 10) was F(2,105) = 2.501; *p* <0.087 and manganese (Tables-11 and 12) was F(2,105) = 4.595; *p* <0.012. The *p* statistics computed for groundwater iron was found to be 0.087; whereas, for groundwater manganese, it was 0.012. These two calculated *p* values on comparison with alpha (α<0.05) reported that groundwater iron results were not statistically significant at this level (0.05); whereas, groundwater manganese was significant at this level and null hypothesis must be rejected.

Table-6: Correlation matrix (Winter)

Particular		Iron	Manganese	pH	TDS	Cl^-
Correlation	Iron	1.000	.084	-.418	-.211	-.161
	Manganese	.084	1.000	-.246	.181	.316
	pH	-.418	-.246	1.000	-.011	-.108
	TDS	-.211	.181	-.011	1.000	.942
	Cl^-	-.161	.316	-.108	.942	1.000
Sig. (1-tailed)	Iron		.312	.006	.108	.174
	Manganese	.312		.074	.145	.030
	pH	.006	.074		.474	.265
	TDS	.108	.145	.474		.000
	Cl^-	.174	.030	.265	.000	

TDS - Total dissolved solids and Cl^- - Chloride, Sig. - Significant.

Table-7: Correlation matrix (Summer).

Particular		Iron	Manganese	pH	TDS	Cl^-
Correlation	Iron	1.000	.243	-.455	-.029	-.010
	Manganese	.243	1.000	-.142	.169	.205
	pH	-.455	-.142	1.000	-.020	-.118
	TDS	-.029	.169	-.020	1.000	.954
	Cl^-	-.010	.205	-.118	.954	1.000
Sig. (1-tailed)	Iron		.077	.003	.434	.477
	Manganese	.077		.204	.163	.116
	pH	.003	.204		.455	.246
	TDS	.434	.163	.455		.000
	Cl^-	.477	.116	.246	.000	

Table-8: Correlation matrix (Post-monsoon).

Particular		Iron	Manganese	pH	TDS	Cl^-
Correlation	Iron	1.000	.040	-.546	-.209	-.131
	Manganese	.040	1.000	-.053	.112	.077
	pH	-.546	-.053	1.000	.187	.058
	TDS	-.209	.112	.187	1.000	.938
	Cl^-	-.131	.077	.058	.938	1.000
Sig. (1-tailed)	Iron		.408	.000	.111	.223
	Manganese	.408		.380	.259	.327
	pH	.000	.380		.138	.369
	TDS	.111	.259	.138		.000
	Cl^-	.223	.327	.369	.000	

Table-9: Descriptive details for one way ANOVA for groundwater iron

Season	n	Mean	SD	Std. Error	95% confidence interval for mean		Minimum	Maximum
					Lower bound	Upper bound		
Winter	36	3.522	9.01	1.364	0.0673	5.609	BDL	47.100
Summer	36	0.730	0.909	0.151	0.423	1.038	0.164	3.825
Post-monsoon	36	0.582	0.920	0.153	0.271	0.894	0.055	4.022
Total	108	4.834	10.839	0.467	0.458	2.309	BDL	47.100

Mean, SD, Std. Error, Minimum and Maximum are reported in mg/L. BDL - Below detection limit, SD - Standard deviation.

Table-10: One way ANOVA for groundwater iron

Heavy metal	Source of variations	Sum of squares	df	Mean square	F	Sig.
Iron	Between groups	114.638	2	57.319	2.501	0.087
	Within groups	2406.085	105	22.915		
	Total	2520.72	107			

df - Degree of freedom, F - F test, Sig. – Significant.

Table-11: Descriptive details for one way ANOVA for groundwater manganese

Season	n	Mean	SD	Std. Error	95% confidence interval for mean		Minimum	Maximum
					Lower bound	Upper bound		
Winter	36	0.257	0.390	0.060	0.078	0.323	BDL	1.853
Summer	36	0.058	0.095	0.015	0.026	0.091	0.003	0.474
Post-monsoon	36	0.058	0.135	0.022	0.012	0.103	0.002	0.761
Total	108	0.373	0.620	0.022	0.060	0.151	BDL	1.853

Mean, SD, Std. Error, Minimum and Maximum are reported in mg/L. BDL - Below detection limit, SD - Standard deviation

Furthermore, mean square between groups and within groups provides information pertaining to sampling variance and analytical measurement variance respectively. From these observations, it can be concluded that sampling variation was more (iron 57.319 and manganese 0.243) as compared with analytical measurement variance (iron 22.915 and manganese 0.053). Thus, it can be concluded that variation in groundwater iron and manganese concentration were originated from a sample rather than analytical measurement variation. Thus, it can be further concluded that errors from analytical measurements were minimum and sampling variation had contributed to analytical measurement. It can also be concluded that spatial variation in groundwater iron and manganese concentration was there from the study area.

One way analysis of variance for iron and manganese in between group and within the group as reported by Oyem *et al.*[23] is in accordance with the findings of this study. Between-group observations were more than within group observations which indicates that variation in iron and manganese concentration was due to sampling variance and not due to analytical measurement variance.

Water source age, depth, Fe and Mn conc.: Correlation between water source age (years), depth of water source (ft bgl) and iron and manganese concentration during winter (Table-13) was found that iron with age and depth of water source was significant at 0.05 level. No correlations were observed between these five variables. In the summer (Table-14) groundwater iron concentration with age of water source was significant at 0.05 level; whereas, manganese with iron was also significant at the same level. Post-monsoon observations pointed out (Table-15), iron with age of water source was significant at 0.05 level, iron and manganese with altitude and age of water source were significant at 0.01 level. Furthermore, from these observations in these tables, it can be stated that the age of water source and iron and manganese concentration was not correlated. The hand pump corrosion which may be an issue of concern as the age of hand pump progresses does not prove from the observations for its contribution to groundwater iron concentration. Thus, it can be stated that the age of water source and groundwater iron concentrations were not correlated with each other. This finding indicates that the source of groundwater iron was of the geogenic origin and may not from hand pump corrosion. The findings are in accordance with Hasan and Ali (2010) that no clear trend between the age of tube-well and manganese concentration[54].

Table-12: One way ANOVA for groundwater manganese.

Heavy metal	Source of variation	Sum of squares	df	Mean square	F	Sig.
Manganese	Between groups	0.485	2	0.243	4.595	0.012
	Within groups	5.547	105	0.053		
	Total	6.032	107			

df - Degree of freedom, F - F test, Sig. – Significant.

Table-13: Pearson's correlation coefficient between water source characteristics (Winter)

	Altitude	Age	Depth	Iron	Manganese
Altitude	1				
Age	0.17196	1			
Depth	0.07183	-0.1707	1		
Iron	-0.0496	-0.2125**	-0.2009**	1	
Manganese	-0.0712	-0.1438	0.03149	0.08414	1

*Significant at 0.01 level; ** 0.05 level.

Table-14: Pearson's correlation coefficient between water source characteristics (Summer)

	Altitude	Age	Depth	Iron	Manganese
Altitude	1				
Age	0.17196	1			
Depth	0.07183	-0.1707	1		
Iron	-0.1388	-0.2129**	0.08912	1	
Manganese	-0.0092	-0.118	0.05821	0.24266**	1

Table-15: Pearson's correlation coefficient between water source characteristics (Post-monsoon)

	Altitude	Age	Depth	Iron	Manganese
Altitude	1				
Age	0.17196	1			
Depth	0.07183	-0.1707	1		
Iron	-0.373*	-0.2392**	-0.0129	1	
Manganese	0.3173*	-0.2686*	-0.033	0.04001	1

*Significant at 0.01 level; ** 0.05 level.

The water source contributing to groundwater iron concentration from wells where casing pipes were very old and corroded was ruled out by Alam and Umar[33]. This observation is in agreement with the findings of the study. Pearson's correlation coefficient for the age of water source and iron and manganese concentration reported negative weak to moderate correlation in all the seasons studied.

Pearson's correlation coefficient between water extraction depth and iron and manganese concentration could not be established which is broadly consistent with Daughney[58]. If groundwater extracted from greater depths were typically and significantly more reducing conditions than shallow groundwater, then a correlation between water extraction depth and metal concentration would be probable. However, lack of correlation between water extraction depth and concentrations of iron and manganese in groundwater indicates that such indirect relationships are not significant.

Conclusion

The PCA carried out on groundwater iron and manganese identified two principal components controlled their variability. Iron and manganese have been included in PC2, which is controlled by lithogenic sources. Cluster analysis of groundwater iron and manganese concentration from winter, summer and post-monsoon showed that maximum sampling locations were forming a major cluster and in some cases, sub-cluster were also observed. The results of this cluster analysis show that major cluster group originates from one source and it can be assigned to geogenic in origin.

In the correlation analysis, it was found that iron and manganese were not significantly correlated with each other. One way analysis of variance (ANOVA) for iron and manganese revealed between group observations were more than within group observations thus variation in iron and manganese concentration was due to sampling variance and not due to analytical measurement variance. Age, altitude, and depth (in general) of water source had no significant correlation with groundwater iron and manganese concentration.

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