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Assessment and processing of groundwater quality from various land uses - a case study in Odisha

Madhumita Das*, A.K. Nayak, O.P. Verma and R. Sethi

ICAR-Indian Institute of Water Management, Bhubaneswar, Odisha.

*Corresponding author:
E-mail: mdas6@yahoo.com (Madhumita Das)

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ABSTRACT

Water quality monitoring is a prerequisite to checking water pollution. To assess the quality, groundwater was collected from seventy-two bored / dug wells spaced 20 to 95 km apart and across the different land uses in Odisha, India. Application of geochemical techniques revealed the prevalence of alkaline earth metals (Ca, Mg) and weak acid (HCO_3) ions in hydrochemical facies formations; and mineral dissolution through rock weathering and base exchange processes. Multivariate statistics were then applied to various water quality parameters to group them through principal components (PCs) and clustering. The water quality index (WQI) was formulated, and the suitability of water was determined, which progressively improved from Cluster I to IV for irrigation and drinking use purposes. The cluster-specific best-fit regressions between WQI and water parameters were established to provide essential parameters for monitoring groundwater quality despite their collection from different land uses.

1. INTRODUCTION

Groundwater provides an assured supply of relatively pure water. It has thus become the major water source for the domestic, irrigation, and industrial sectors. India is the largest user of groundwater, with annual withdrawals of approximately 88% of the water used for irrigation and ≥ 85% for rural drinking water (IDFC, 2013; CGWB, 2010). The rapid expansion of urban areas, industrialization, mining, and developmental activities, concurrent with the rising demands of exploding population and the increasing diversity of water uses, serve to increase groundwater usage over time, which reduces recharge areas and compromises groundwater suitability for use by the increasing outflow of various wastes. Deterioration of groundwater quality threatens the human health and economic prosperity of a region (Subramani *et al*., 2005; Schiavo *et al*., 2006). Degradation of water quality because of seepage from landfills and swamp pits and discharge of untreated industrial effluents and municipal sewage have been reported in many cities and industrial centers (Biswas and Sharma, 1995). A gradual decline in groundwater quality caused by high TDS and salinity has been encountered with increasing pumping depths in north Gujarat (Kumar *et al*., 2004). The impact on groundwater fitness of domestic, industrial, and agricultural wastes, run-off from urban areas, and soluble effluents has been reported from Pune (Maharashtra) and Delhi (Wagh *et al*., 2014; Singh, 1999; Adhikary *et al*., 2014). Urbanization and industrialization have been observed to impact groundwater quality in many ways in and around Indian cities. Consequently, the monitoring of groundwater quality has gained importance and increased in scale where water quality is an issue due to the substantial deterioration of the environment and human health.

Water quality monitoring is a prerequisite for water safety and security, particularly for the underground aquifer, which is not limited by state boundary or regional circumference. Moreover, owing to the fact that deterioration of groundwater quality may affect a range of populations and localities. Groundwater quality monitoring is, therefore, imperative for the sustainable existence of progressing urban settlements and industrial areas. Nevertheless, in some places, it is often undone due to its complicacy and infrastructural inadequacy. However, applying statistics, including multivariate statistical techniques, may make water quality monitoring simple, precise, and useful if it targets a large area.

Odisha, located in the eastern part of India, is known for its rich mineral sources, which motivate the establishment of various industries and related services across the state. The urbanization trend in Odisha is illustrated by the fact that only 3% of the total population lived in the cities in 1941, while 2011 census data indicate that the entire population living in cities has increased to 16.68% (www.urbanodisha.gov.in). During the course of development activities, land uses are altered, and the quality of resources is impacted; however, the extent of the impact is determined by the intensity of these activities and their area of influence in a given environment and time. The impact of developmental activities on the enhanced presence of ion concentrations and TDS in shallow and deep underground aquifers over the years has been reported by Li *et al*. (2015). In Odisha, overall groundwater development is only 28.33%, with a wide range of variation from <10 to >50% in some places (www.dowrorissa.gov.in). The probability of contamination of shallow phreatic aquifers by the seepage of run-off water owing to the steep rate of progress due to urbanization and industrialization across Odisha has been mentioned by several workers (Srivastava *et al*., 2002; Srivastava *et al*., 2008; Das *et al*., 2010; Das, 2013; Srivastava *et al*., 2014; Das *et al*., 2018). Realizing the importance of groundwater quality, this investigation was undertaken to study the groundwater quality of various land uses and refine the information to a level enabling effective determination of the water quality in a case study in Odisha, India.

2. MATERIAL AND METHODS

Study Area

The Indian State of Odisha, located on the eastern fringe of peninsular India, receives 1500 mm of annual rainfall (average) from July to September. The study areas were selected based on distinct variations in land-uses; and the intensity of groundwater use for irrigation, drinking, and domestic purposes. Twenty-one samples were taken from the Jagatpur industrial estate (JIE) and 20 from the Khorda industrial area (KIA); those areas have come up because of convenience and well connectivity to Bhubaneswar, the capital city of Odisha. Next, 19 samples were collected from Haripur, where an agro-industry, *i.e.* sugar mill, has developed owing to the availability of a large farm area for sugarcane cultivation, and 12 from the Pandua area, which is not only away from the city but free from industrial / developmental activities as well. All four areas cover portions of the state's adjoining Cuttack, Khorda, and Dhenkanal districts. JIE is on the banks of the Mahanadi River. Haripur is located at the Dhenkanal block, around 6 km from the district headquarters, while Pandua is at the interior of the Kamakhyanagar block (Table 1).

The JIE is in the southern part of the Cuttack district on the Athgarh formation of the Gondwana super-group. In Khorda, outcrops of the Gondwana super-group mostly occur in clusters that form uplands in the north-eastern part of the district and are represented by a conglomerate, gritty sandstone, occasionally pebbly, siltstone and clay that belong to the Athgarh formation of the upper Gondwanas. The earliest Quaternary deposit occupies the central and northern parts of the district and comprises hard crust laterite, latosol, and residual soil. Dhenkanal district is occupied by various lithostratigraphic units with varied assemblages: the oldest units are Singbhum Granite and the Gorumahishani group of Archaean age. Laterization is common in the north, mostly thick and ferruginous. Residual soil and alluvium, with or without intermittent

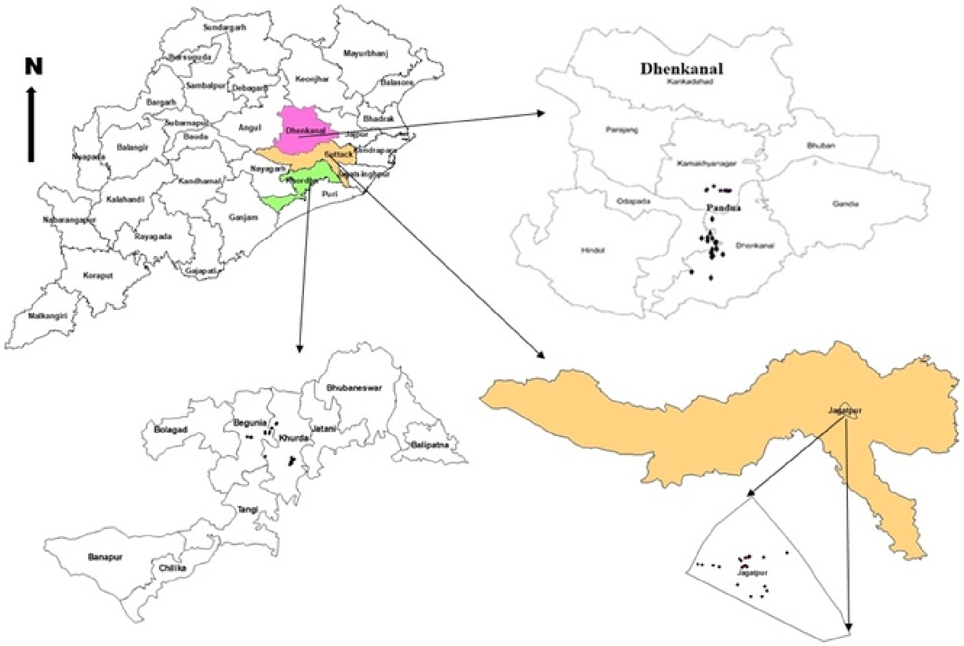


Fig. 1. Locations of study areas in Cuttack, Dhenkanal and Khordha districts of Odisha

Table: 1
Brief description of the study areas

Detail of the study areas				ACZ*	Latitude	Longitude	Area (km^2)
Locations	Block	District	Description				
Pandua	Kamakhyanagar	Dhenkanal	Farming is the major land use	Mid central table land	20°79` to 20°80`N	85°54` to 85°59`E	0.1624
Haripur	Dhenkanal	Dhenkanal	Sugar mill, distillery unit, and farming	Mid central table land	20°58` to 20°78`N	85°51` to 85°58`E	2.724
Jagatpur industrial estate (JIE)	Cuttack Sadar	Cuttack	Food processing, beverages, board making units and urban land use	East and south eastern coastal plain	20°48` to 20°49`N	85°92` to 85°95`E	0.1819
Khorda industrial area (KIA)	Khorda	Khorda	Beverages units and farming	East and south eastern coastal plain	20°10` to 20°21`N	85°48` to 85°61`E	2.127

**Agro-climatic zone*

laterite, cover the banks of the Brahmani river and the river basin (www.orissaminerals.gov.in).

Collection and Analyses of Samples

Seventy-two samples were collected from dug and bored wells in white polyethylene sample bottles pre-washed with diluted acid, rinsed with distilled water, and air-dried during the pre-monsoon period (April-May 2016). The sample was collected from the sources where the local people have majorly used it following a random sampling technique. Each sample was collected in three separate containers for the analysis of heavy metals (100 ml water in 0.3 ml ultra-pure HNO_3), NO_3 (100 ml water in 2 ml of ultra-pure H_2SO_4), and 500 ml water for the estimation of other relevant parameters. The samples were analyzed for electrical conductivity (EC), pH, total dissolved solids (TDS), major cations (sodium, potassium, calcium, magnesium), anions (bicarbonate, chloride, sulfate, nitrate), iron, copper, zinc, manganese, cadmium, lead, and chromium following standard methodologies (APHA 1995). In addition, EC and pH were measured *in-situ* just after collecting the samples.

Geochemical Evaluation of Water Quality

The analyzed values of the major cations (Na, K, Ca, Mg) and anions (Cl^-, HCO_3^-, SO_4^{-2}) were employed to draw Piper trilinear diagrams (Piper, 1944) using AQUACHEM software (AquaChem 11.1) to identify the hydrochemical facies present in the samples (Fig. 2). Gibbs plots, chloro-alkaline indices (CA I and CA II) and various ion ratios were computed following standard procedures to identify the respective factors and processes that determine the geochemistry of groundwater and its suitability for drinking and irrigation purposes.

Statistical Analyses

To reduce the dimensionality in the data structure, principal component (PC) analysis was performed for 23 water quality parameters. Five PCs were extracted with eigenvalues >1.0; the regression scores of the components were analyzed through agglomerative hierarchical clustering following Ward's method and the squared Euclidean distance for the dissimilarity test, which produced nested clusters of seventy-two samples (Fig. 4) and was classified by K-means clustering following the elbow method to four clusters.

The samples were rearranged into respective clusters I, II, III, and IV, and descriptive statistics (max, min, mean and std. deviation) of the water quality data were carried out for each cluster.

Computation of the Water Quality Index (WQI)

The groundwater quality was assessed by comparing parameters with the standard water quality guidelines respective to drinking and irrigation uses (Table 3). First, the WQI was computed following the methodology given by Batabayl and Chakrabarty (Batabyal *et al*., 2015). In that methodology, some weight (*wi*) was allotted to individual parameters according to their significance for determining water quality, either for drinking or irrigation use, which varied from 1 (slight) to 4 (considerable), and the relative weight (*Wi*) of the parameter was determined:

$$Wi = \frac{\mathrm{wi}}{\sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{wi}}$$

Where, *Wi* is the relative weight, *wi* is the weight of the individual parameter, and *n* is the number of parameters.

A quality rating for each parameter is then generated, dividing its concentration by its respective standard value, and the result is multiplied by 100.

$$qi = \left(\frac{\mathrm{Ci}}{\mathrm{Si}}\right) 100$$

Where, *qi* is the quality rating of parameter *i, Ci* is the measured concentration of the i^{th} parameter, and *Si* is the respective standard value given by the BIS (2012) and WHO (2011) for drinking and the BIS (1986), Ayers and Westcot (1985), AICRP annual report (1990 - 1992) and Das (1998) for irrigation purposes.

A sub-index for individual parameters was obtained by multiplying *Wi* by *qi*. Therefore, *SIi = Wiqi* and

$$\text{WQI} = \sum_{i=1}^{n} \text{SIi}$$

Where, *SIi* is the sub-index of the i^{th} parameter and WQI is the summation of *SIi* of *n* number of water quality parameters. The WQI computed for drinking and irrigation purposes is classified into four categories: Excellent ≤ 25, good 25 - 50, poor 50 - 100, unsuitable >100.

Sensitivity Analysis

Pearson's correlation coefficient between cluster-specific WQIs and respective water quality parameters was carried out. In addition, the best-fit regression was calculated to discover the sensitive variables for the respective WQI for drinking and irrigation purposes. The results are presented in Table 5. All statistical analyses were carried out in XLSTAT (www.xlstat.com).

3. RESULTS AND DISCUSSION

Groundwater samples were collected from depths varying from <3.05 to 30.5 m in JIE, 9.14 to 91.44 m in the KIA and Haripur (Dhenkanal), and <15.24 to 60.96 m in the Pandua (Dhenkanal) area. Water was characterized as Na > Mg > Ca >> K and Cl > HCO_3>SO_4 in JIE, Na > Ca > Mg >> K and Cl >HCO_3>SO_4 in (KIA), Na > Ca > Mg >> K and Cl > SO_4 > HCO_3 in Haripur and Na Ca > Mg >> K and SO_4 > Cl > HCO_3 types in Pandua. In addition to the major ions' concentrations, Fe and Mn and traces of Zn were observed, while no traces of nitrate, phosphate, Cd, Cr, and Cu were found in the samples.

Geochemical Characterization

Jagatpur Industrial Estate (JIE)

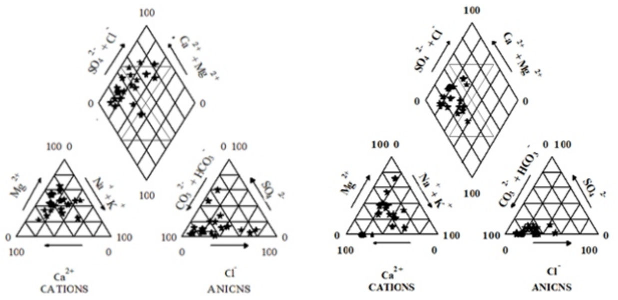
The piper trilinear diagram reveals that Mg represents 33% of samples - Ca - HCO_3, 29% by Mg -Ca - HCO_3 - Cl, and 9% each by Mg - Na - Cl -HCO_3, Mg - Ca - Na - HCO_3 - Cl, and mixed hydrochemical facies, such as Ca - SO_4 - HCO_3, Mg - Na - Ca - Cl, Na - HCO_3 - Cl - SO_4 and Mg - HCO_3 - SO_4 (Fig. 2). The variation of Gibbs ratios I and II with the log of TDS (mg L^{-1}) reflects the importance of rock dominance (77% sample) for the dissolution of aquifer minerals (Fig. 3). The ion exchange between groundwater and its host environment during residence time and movement can be determined by examining the chloroalkaline indices, *viz.,* CAI and CAII, described as [Cl - (Na + K)] / Cl and [Cl - (Na + K)] / (SO_4 + HCO_3 + CO_3). If Na and K are exchanged with Mg or Ca ions in water, the index value will be positive, indicating base exchange (88%), whereas low salt water gives negative values, indicating chloroalkaline disequilibrium, *i.e.,* reverse ion exchange (Adrian *et al*., 2007), as is evident in 12% of the samples.

Khorda Industrial Area (KIA)

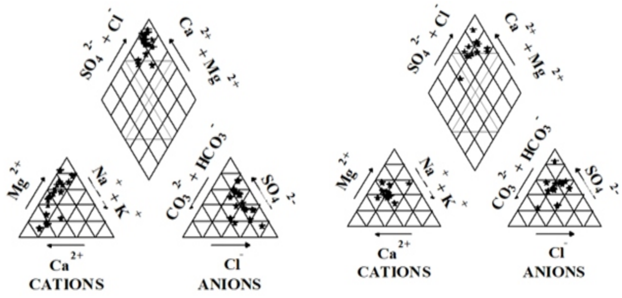
The sample can be characterized as Ca - Na - Mg - HCO_3 - Cl (45%) > Na - Ca - Cl - HCO_3 (30%) > Na - Cl (15%), with a meager representation of Na - Cl - SO_4 - HCO_3 and Ca - Na - Mg - Cl hydrochemical facies types (Fig. 2). The Gibbs diagrams indicate that the dissolution of minerals from rocks is the major geochemical process. The chloroalkaline indices (CAI and CAII) become negative in 77% of samples, indicating chloroalkaline disequilibrium, and positive in the remaining 30% of samples, indicating the exchange of Na in groundwater with Ca or Mg from the aquifer substrate.

Haripur

Approximately 21% of the water samples were found to be represented by Ca - Na - HCO_3 - Cl, Na - Ca - Cl - HCO_3, and Na - Cl - HCO_3, with an inadequate presence of mixed hydrochemical facies, *viz.,* Ca - Cl - HCO_3, Ca - Mg - Na - Cl, Na - Cl - HCO_3 - SO_4, Na - Cl, and Na - Cl - SO_4 - HCO_3 (Fig. 2). The distribution pattern of the Gibbs ratios reveals that host rocks are the major source of water chemistry (Fig. 3) and that base exchange is the only ion exchange process, as evident from the chloroalkaline indices.

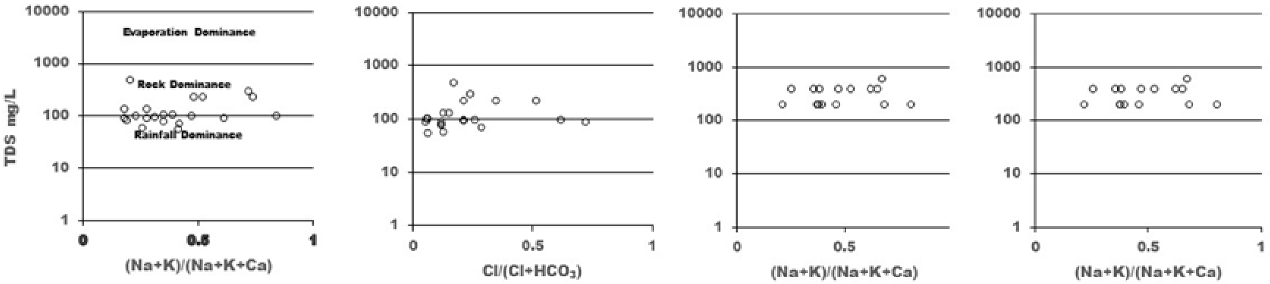


Jagatpur industrial estate *Khorda industrial area*



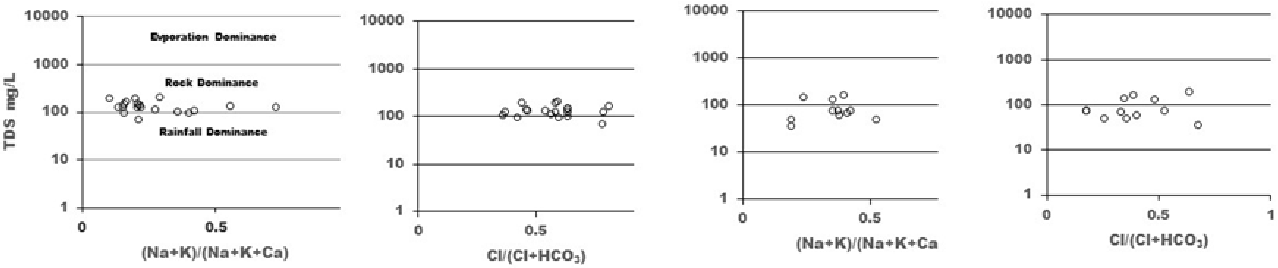
Haripur *Pandua*

Fig. 2. Piper diagrams of the groundwater collected from four different landforms in Odisha



Jagatpur Industrial Estate (JIE)

Khorda Industrial Area (KIA)



Haripur

Pandua

Fig. 3. Gibbs diagram for dominating geological processes in collected water samples from study areas

Table: 2
Estimates of ion ratios in groundwater

Ion ratios	Values	Percent of samples in different locations			
		JIE	KIA	Haripur	Pandua
Ca / Mg	=1.0	52.0	35.0	31.6	33.33
	>2.0	9.5	35.0	31.58	16.67
Na / Cl	<1.0	90.47	65.0	100.0	100.0
	>1.0	9.5	35.0	0	0
Na+K / Ca+Mg	>1.0	4.76	35.0	0	8.33
Ca+Mg / HCO_3	<1.0	0	25.0	94.74	100
Ca+Mg / HCO_3+SO_4	<1.0	23.8	57.89	0	75.0
	≅1.0	47.62	40.0	5.26	25.0
	>2.0	28.57	0	94.74	0

Pandua

Based on the Piper diagram, 42% of samples are represented by Mg - Ca - Cl - SO_4, 25% by Mg - Ca - HCO_3 - SO_4 - Cl, and 16% by Mg - Na - Ca - HCO_3 - Cl and mixed hydrochemical facies types (Na - SO_4 - HCO_3 - Cl, Mg - Cl - HCO_3), and rock dominance followed by rainfall dominance were found to be contributing factors for determining water chemistry. As in the case of Haripur groundwater, the base exchange is the key ion exchange process based on the chloroalkaline indices (CAI and CAII); thus, $CaHCO_3$ and $MgHCO_3$, followed by mixed $CaNaHCO_3Cl$ in JIE and KIA, and CaCl, followed by a slight presence of mixed $CaNaHCO_3Cl$, are found to dominate ion compositions in the Haripur and Pandua areas, respectively.

Ion ratios

Different molar ratios of cations and anions were computed to identify the respective geochemical processes contributing to the groundwater composition (Table 2). In a majority of samples, the Na / Cl molar ratio was <1.0, *e.g.,* 100% in Haripur and Pandua, and from 65% to 90% in the rest of the locations (JIE, KIA), indicating the result of cation exchange (Wayland *et al*., 2003). At the same time, the increase in the ratio (>1.0) is typically interpreted as Na release from silicate weathering (Meybeck, 1987), as evidently shown in the 9.5% to 35% samples from JIE and KIA, respectively. Excess Na may also result from a wastewater effect due to anthropogenic activities during water movement through the aquifer (Vengosh and Keren, 1996). The (Ca + Mg) / HCO_3 molar ratio varied from 0.77 to 7.93. A low ratio (1.0) indicates the dissolution of carbonate minerals through intense weathering, as observed in 95% to 100% of the samples in Haripur and Pandua and only 25% of the samples in KIA, while a high ratio (>2.0) indicates other sources of Ca + Mg as a result of a reverse ion exchange process in 40% of samples overall (Srinivasamoorthy *et al.*, 2011). A binary ion ratio of (Ca + Mg) / (HCO_3 + SO_4) of <1.0 indicates the replacement of Ca + Mg by reverse ion exchange in 24%, 58%, and 75% of samples in JIE, KIA, and Pandua, respectively, and 1.0 indicates the dissolution of calcite, dolomite and gypsum (McLean *et al.*, 2000) in 48%, 40%, 5% and 25% of samples in JIE, KIA, Haripur, and Pandua, respectively. A high molar ratio (>2.0) reflects reverse ion exchange, resulting in Ca + Mg enrichment in 28% and 90% of samples in JIE and Haripur, respectively.

The host rocks are the primary sources of dissolved solids, and normal ion exchange (*i.e.,* base exchange) is the dominant process in groundwater, whereas reverse ion exchange is also observed in some samples. The geochemical evaluation of groundwater reveals the basic nature of groundwater constituents that vary with the rate of evaporation and the amount of rainfall received for a particular period of observation.

Statistical Analyses

The nitrate, copper, cadmium, lead, and chromium in the waters were at non-detectable levels, while sodium adsorption ratio (SAR) is required only for irrigation water quality appraisal. Therefore the PC analysis of fourteen standard water quality parameters *viz.,* EC, pH, Na, K, Ca, Mg, Fe, Mn, TDS, Cl, HCO_3, SO_4, Mg / Ca, and Cl / SO_4 (Table 3); and nine geochemical parameters, *e.g.* Na / (Na + Mg), Ca / Mg, Na / Cl, (Na + K) / (Ca + Mg), (Ca + Mg) / HCO_3, Na / Ca, Ca / Cl, Chloroalkaline indices I and II) was performed. It resulted in five PCs with eigenvalues >1.0, contributing 86% of the variability in the data. The first PC_1 showed highly significant correlations ($p>0.001$) with pH, Na, K, Ca, Mg, Cl, HCO_3, TDS, and other parameters, PC_2 with EC, PC_3 with Ca / Mg, and PC_4 with SO_4. The level of significance of the water parameters with PCs generally decreased from PC_1 to PC_5.

A dendrogram was formed (Fig. 4) using regression scores of the PCs, which revealed the probability of alliance among the observations through nested clusters. K-means clustering led to the classification of the samples into four definite clusters. The numbers of samples grouped into clusters C_I, C_{II}, C_{III}, and C_{IV} were 7, 43, 13, and 9, respectively. The cluster-wise presentation of water quality parameters in Table 4 indicates that the pH (mean) was acidic (5.92) to neutral (7.49) in reaction across the clusters. Besides, the high value (mean) of EC (0.64 dS m^{-1}), Na (2.23 meq L^{-1}), Mg (3.64 meq L^{-1}), Cl (2.34 meq L^{-1}), and Mn (0.45 mg L^{-1})

Table: 3
Water quality standards and the weight assigned to different parameters

Parameters	Water quality standards			
	Threshold levels for drinking water (WHO 2011)	Assigned weight (wi) to drinking water quality parameters	Threshold levels for irrigation water	Assigned weight (wi) to irrigation water quality parameters
pH	6.5-8.5	4	6.5-8.5	3
EC dS m^{-1}	-		0-4.0	4
Na (mg L^{-1})	0-50	2	0-150	3
K (mg L^{-1})	- 10-12[c]	1	-	
Ca (mg L^{-1})	100-300, 75-200[a]	2	-	
Mg (mg L^{-1})	30-100[a]	2	-	
Chloride (mg L^{-1})	200-300, 250-1000[a]	3	75-350	4
HCO_3 (mg L^{-1})	- 244-732[b]	3	-	
TDS (mg L^{-1})	600-1000 500-2000[a]	4	-	
SAR (mM L^{-1})$^{0.5}$	-		0-10.0	4
SO_4^{-2} (mg L^{-1})	- 200-400[a]	3	-	
Zn (mg L^{-1})	4.0, 5.0-15[a]	2	0-2.0	1
Fe (mg L^{-1})	0.3	3	0-5.0	2
Mn (mg L^{-1})	0.1-0.4 0.1-0.3a	3	0-0.2	2
Mg/Ca	-		0-3.0	2
Cl/SO_4	-		0-2.0	2

[a] *Threshold level recommended by IS 10500 : 2012;* [b] *Threshold level recommended by Bureau of Indian Standards (1991) Indian Standard Drinking Water-Specification. 1st rev. Bureau of Indian Standards: New Delhi, India;* [c] *European Commission*

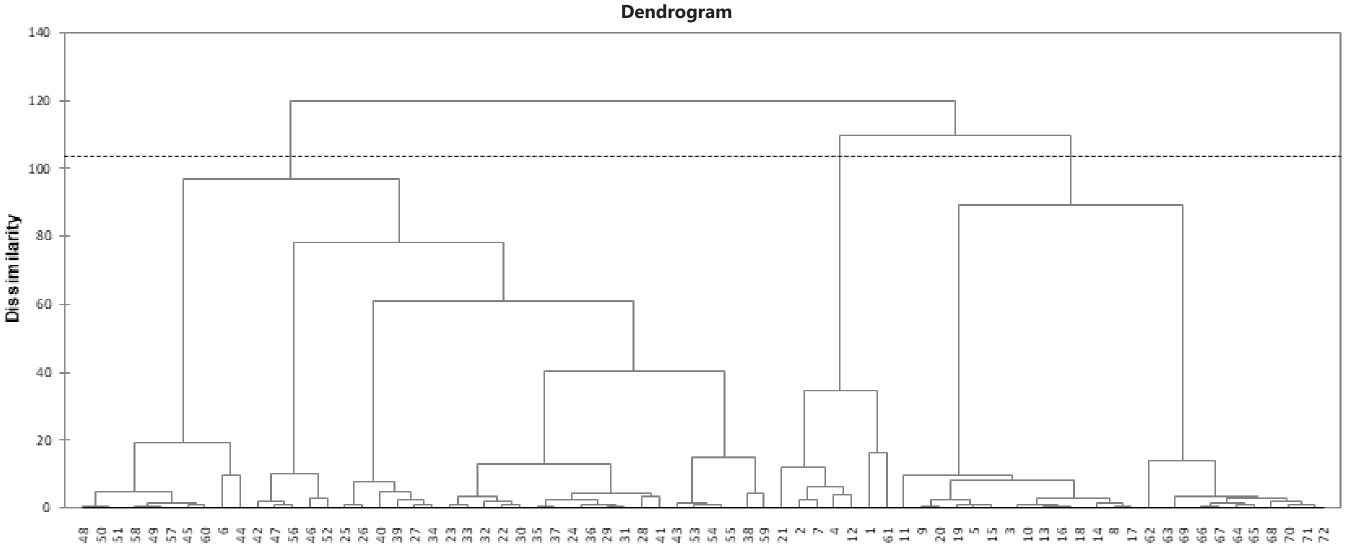


Fig. 4. Nested clusters of seventy-two sites covering four different landforms

in C_I, Ca (1.94 meq L^{-1}), HCO_3 (2.55 meq L^{-1}) and TDS (182.1 mg L^{-1}) in C_{II} were recorded.

Water Quality Assessment

The standards recommended by the WHO (2011) and BIS (2012) for evaluating water quality for drinking were employed. Irrigation water quality is, however, mainly determined by pH, EC, SAR, and residual sodium carbonate (RSC). In addition, the beneficial and toxic effects of ion ratios (Ca/Mg, Cl/SO_4) and the threshold levels of heavy metals and other elements have been reported from various locations. Considering all of these guidelines, the threshold levels of the water quality parameters recommended for conventional irrigation practices in field crops are documented in Table 3.

Based on the WQI scale, the percent increase of samples classified as 'excellent' is 0 to 66 and 0 to 55, and the decrease in samples in the 'unsuitable' category is 28 to 0, and 43 to 0 from C_I to C_{IV} for drinking and irrigation use, respectively (Fig. 5). Water quality in C_{II} and C_{III} largely remained 'good' (WQI, 25.0 - 50.0) and 'poor' (WQI, 50.0 - 75.0), respectively for both the uses.

Pearson's correlation coefficient was highly significant ($p<0.01$) among WQI and pH, Na, Mg, Cl, Fe, and Mn and among Na, Fe, and Mn in cluster I (Table 5). Na, Cl, and Mn invariably showed significant levels for Pearson's - r with respect to the WQI in all clusters (C_I to C_{III}) except C_{IV} for both uses. A highly significant relationship between Fe and the corresponding WQI was noted in C_I, $C_{II,}$ and $C_{IV,}$ and C_I and C_{II} for irrigation and drinking use, respectively. The HCO_3 and TDS revealed highly significant r - values with the corresponding WQI for C_{II} to C_{IV} for drinking. The best-fit regression was then used to identify the sensitive water quality variables for determining WQI for the respective clusters and water uses.

The data pertaining to the best-fit regression equation for drinking WQI in Table 6 indicate the significance of Fe for determining water quality from C_I to C_{III}. The coefficient of Fe was 68.54 to 199.45 times higher than other corresponding water quality parameters. High concentrations of Fe in phreatic shallow aquifers have been reported from various locations in Odisha (Das *et al*., 2001). Fe is one of the major elements in the lateritic soil type. Of the 15.57 M ha total geographical area of Odisha, a 13.3 M ha area is covered with red, mixed red and yellow, and lateritic soil types and characterized by low pH and a high Fe and Mn content (Sahu and Mishra, 2005), which may explain the large contribution of Mn to groundwater quality in C_{II} to C_{IV} with respect to their irrigation WQIs. The sporadic presence of Mn in underground aquifers in the capital city of Odisha was reported by Das *et al*. (2018). Odisha is rich in various mineral resources. Vast deposits of Fe and Mn ore are located in the northern part of the state (Mohapatra *et al*., 2009), which may be attributed to their contribution to groundwater chemistry (Dash *et al*., 2016). The key parameters have thus evolved from best-fit regressions respective to different clusters. By determining those parameters, water quality can be assessed periodically for drinking and irrigation purposes.

4. CONCLUSIONS

Water quality monitoring is imperative owing to the emerging threat of groundwater pollution and its impacts on society and the environment. Analyses of various parameters, however, provide the chemical makeup of water; geochemical characterization reflects the nature of processes that govern the elemental concentration in the groundwater

Table: 4
Cluster-wise descriptive statistics of water quality parameters

Parameters	Cluster I				Cluster II				Cluster III				Cluster IV			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	5.30	8.31	6.55	1.08	6.08	8.24	7.10	0.66	6.42	7.95	7.49	0.43	5.54	6.92	5.92	0.41
EC (dS cm^{-1})	0.11	1.05	0.64	0.30	0	1.92	0.49	0.46	0.03	1.40	0.52	0.46	0.11	1.55	0.43	0.45
Na (meq l^{-1})	0.41	5.21	2.23	2.01	0.17	3.10	0.78	0.59	0.10	5.22	0.71	1.37	0.19	0.49	0.37	0.09
K (meq l^{-1})	0.02	0.08	0.05	0.02	0	1.80	0.21	0.40	0.01	0.24	0.07	0.06	0	0.12	0.06	0.04
Ca (meq l^{-1})	0.22	3.81	1.17	1.32	0.71	6.19	1.94	1.01	0.48	2.38	0.75	0.51	0.66	1.76	1.17	0.38
Mg (meq l^{-1})	1.67	6.66	3.64	1.87	0	1.00	2.42	2.27	0.54	2.38	0.82	0.49	0	0.88	0.337	0.27
Cl-(meq l^{-1})	0.40	7.60	2.34	2.54	0.31	4.00	0.94	0.69	0.40	5.60	1.05	1.38	0.30	0.80	0.46	0.15
HCO_3-(meq l^{-1})	0.20	7.04	1.95	2.36	0.11	6.16	2.55	1.81	0.28	10.56	1.49	2.74	0.10	1.76	0.69	0.65
SO_4^{-2}(meq l^{-1})	0.04	2.91	0.91	0.95	0.02	3.34	0.49	0.53	0.46	7.54	1.93	1.92	0	0.74	0.40	0.26
TDS (mg l^{-1})	92.0	230.0	164.0	48.87	0	600.0	182.1	139.0	35.0	300.0	102.83	71.32	0	400.0	145.75	110.1
Zn (mg L^{-1})	0	0.43	0.18	0.18	0	1.98	0.44	0.51	0.04	1.67	0.74	0.464	0	0.96	0.36	0.333
Fe (mg L^{-1})	0	0.43	0.14	0.19	0	0.62	0.14	0.20	0	0	0	0	0	0.02	0.005	0.009
Mn (mg L^{-1})	0	1.61	0.45	0.62	0	1.28	0.36	0.47	0	1.40	0.31	0.42	0	0.20	0.06	0.06
Na/(Na+Mg) mg L^{-1}	0.19	0.74	0.45	0.20	0.03	1.00	0.34	0.18	0.20	0.71	0.46	0.14	0.48	1.00	0.72	0.19
Ca/Mg	0.15	0.57	0.32	0.13	0	5.80	1.40	1.01	0.89	2.29	1.50	0.40	0	11.69	4.42	3.37
Mg/Ca	1.75	6.59	3.66	1.58	0	3.26	0.99	0.68	0.44	1.12	0.72	0.20	0	0.84	0.26	0.24
Na/Cl	0.03	1.31	0.46	0.48	0.011	2.00	0.56	0.49	0.004	1.13	0.11	0.31	0.02	0.84	0.30	0.36
(Na+K)/(Ca+Mg)	0.39	1.11	0.66	0.27	0.046	2.96	0.58	0.75	0.15	1.15	0.50	0.26	0.22	0.91	0.50	0.24
(Ca+Mg)/HCO_3	0.06	3.66	1.31	1.46	0.108	7.93	1.75	1.49	0.01	2.43	0.22	0.66	0.05	1.65	0.66	0.66
Na/Ca	1.23	6.05	3.51	1.58	0.108	3.08	0.92	0.76	0.23	4.39	0.88	1.08	0.27	1.24	0.55	0.31
Ca/Cl	0.14	0.62	0.31	0.17	0.347	4.87	1.24	1.09	0.26	0.79	0.55	0.17	0.67	2.92	1.54	0.65
CA I	-1.07	56.72	16.25	18.85	-3.35	28.36	5.44	8.92	3.41	35.80	21.14	8.62	-0.60	21.62	9.17	8.05
CA II	-0.21	32.33	11.99	12.65	-0.727	24.40	3.70	5.82	-0.28	66.49	37.39	18.31	0.06	18.91	8.69	7.55

CA I and II are Choloroalkaline indices

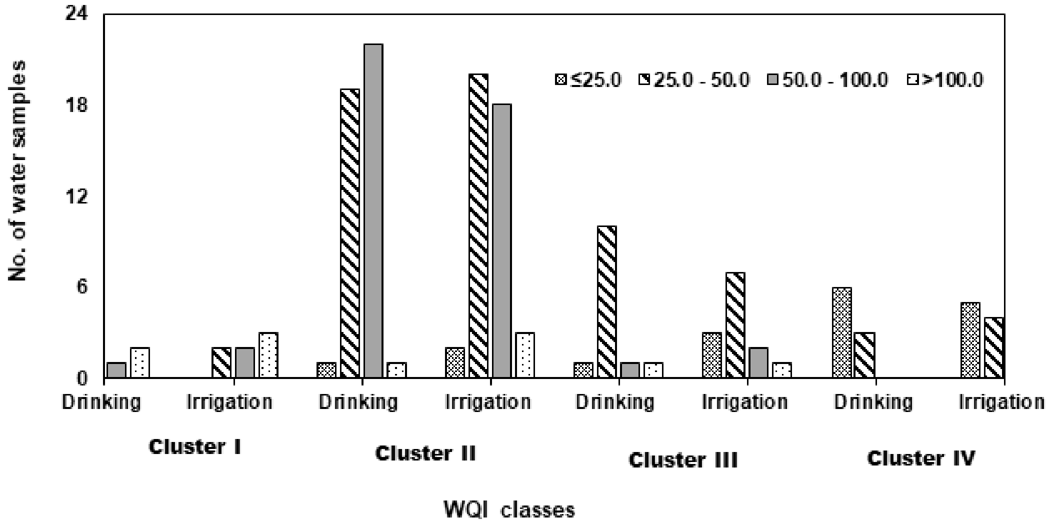


Fig. 5. Cluster-wise WQI for drinking and irrigation purposes

Table: 5
Simple correlations (r-values) between water quality index (WQI) and water parameters

Variables	WQI for drinking				Variables	WQI for irrigation			
	Cluster I	Cluster II	Cluster III	Cluster IV		Cluster I	Cluster II	Cluster III	Cluster IV
pH	0.91^{b}	0.36^{a}			pH				
Na (mg L^{-1})	0.99^{b}	0.64^{b}	0.90^{b}		EC (dS m^{-1})				
K (mg L^{-1})		0.48^{b}	0.70^{b}		Na (mg L^{-1})	0.85^{b}	0.41^{b}	0.79^{b}	
Ca (mg L^{-1})	0.81^{a}	0.51^{b}	0.96^{b}		Cl(mg L^{-1})	0.79^{a}	0.56^{b}	0.80^{b}	
Mg (mg l^{-1})	0.97^{b}	0.37^{a}	0.87^{b}		Zn (mg L^{-1})			-0.58^{a}	
Cl (mg L^{-1})	0.87^{b}	0.49^{b}	0.86^{b}		Fe (mg L^{-1})	0.89^{b}	0.46^{b}		0.77^{b}
HCO_3(mg L^{-1})		0.44^{b}	0.94^{b}	0.67^{b}	Mn (mg L^{-1})	0.89^{b}	0.59^{b}	0.85^{b}	
SO_4 (mg L^{-1})		0.38^{b}	0.63^{a}		SAR (mM $L^{-1})^{0.5}$		0.30^{a}	0.68^{b}	
TDS (mg L^{-1})		0.43^{b}	0.78^{b}	0.95^{b}	Mg/Ca				
Zn (mg L^{-1})					Cl/SO_4		0.64^{b}		0.77^{b}
Fe (mg L^{-1})	0.97^{b}	0.57^{b}							
Mn (mg L^{-1})	0.93^{b}	0.49^{b}	0.56^{a}						

^{a} and ^{b} are the level of significance at p 0.05 and 0.01

Table: 6
Parameters of best-fit regressions for WQIs

Cluster id	Intercept	Coefficient of water quality variables (mg L^{-1}) for drinking						Goodness of fit	
		Na	K	Mg	Fe	HCO_3	TDS	R^2	F statistics, level of significance
I	7.89	0.35		0.59	40.44			0.99	84.04, p=0.012
II	26.85		0.87	0.31	61.83			0.86	78.89, p<0.0001
III	25.59	1.23			110.81	0.11		0.99	313.26, p<0.0001
IV	16.55			0.41		4.69	0.32	0.92	16.34, p=0.01

Cluster id	Intercept	Coefficient of water quality variables for irrigation						R^2	F statistics, level of significance
		pH	EC (dS m^{-1})	Na (mg L^{-1})	Cl (mg L^{-1})	Cl/SO_4	Mn (mg L^{-1})		
I	155.01	-25.17		1.55		3.05		0.99	608.87, p = 0.002
II	19.51				0.19	3.47	35.43	0.99	1081.36, P<0.0001
III	-1.14	2.86	8.24				36.02	0.99	274.85, p<0.0001
IV	16.52		6.54		0.22		35.12	0.99	800.85, p<0.0001

system. Standardizing the data through PC analysis reduced the dimensionality, and clustering provided the samples of similar characters. The cluster-specific WQI subsequently revealed the degree of suitability of the samples, derivation of the best-fit regression functions between WQI and corresponding water quality variables eventually disclosed the relative importance of the parameters for determining groundwater quality for drinking and irrigation use purposes. This can be extrapolated to cluster groundwater from various land uses and indicate variables for monitoring water quality for its intended use/s.

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