INVESTIGATION ON THE HYDRO CHEMICAL CHARACTERISTICS OF GROUND WATER SYSTEM OF KADALUNDI RIVER BASIN, KERALA, INDIA

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Abstract

Hydro geochemical characteristics of ground water samples in Kadalundi river basin have been investigated to identify the salination process. The classification of ground water facies was done through piper plot and Durov diagram. The results of analysis showed that the ground water is highly enriched with Na^+ and Cl^{-}, an indication of sea water intrusion in to the ground water as also supported from the Na-Cl signature on the piper diagram. Na-Cl, Na SO_4 and Ca-HCO_3 are the major facies identified from Durov plot. The chemical composition of the ground water is characterized by high variations in anion and cation concentrations due to ion exchange reactions between ground water and sea water components. Irrigational water quality studies on the present ground water samples using Wilcox diagram shows that some of them are poor for irrigational purposes due to salinity.

Key words: correlation coefficient, hydro geochemical processes, irrigational parameters Kadalundi river, piper diagrams, water types.

INTRODUCTION

The quality of ground water is a result of all the processes and reactions that act on the water from the moment it condensed in the atmosphere to the time it is discharged by a well and varies from place to place with the depth of water table (Muhammed Naeem et al., 2007). Groundwater is used for domestic and Industrial water supply and irrigation all over the world. In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population. Human health is threatened by most of the agricultural development activities particularly in relation to excessive application of fertilizers and unsanitary condition. Rapid urbanization, especially in developing countries like India, has affected the availability and quality of ground water due to its over exploitation and improper waste disposal, especially in urban areas. According to World Health Organization, out 80% of all the diseases in human beings are caused by water.

Groundwater quality deterioration could be due to seawater intrusion and over exploitation can be one of the reasons (Aris et.al.2007). Sodium and Chloride are the most abundant constituents in sea water and thus enrichment of these ions in ground waters is an indicative of saline water intrusion in coastal areas (Panteleit et al.,2001). The objective of the present work is to discuss about various hydro geochemical processes occurring in the ground water samples especially in coastal areas and collect evidences for the possibility of sea water intrusion into them.

Methods

Study area

Kadalundy river has a length of 130 km and a drainage area of 122 km^2. Olipuzha and Velliyar are its main tributaries. The downstream stretch of the rivers falls in to Arabian Sea. The river flows through Melattoor, Pandikkad, Malappuram, Panakkad, Kooriyad, and Thirurangady. There is saline intrusion to Kadalundy river system from Arabian sea. This affect groundwater samples near to it. The present study focuses on the hydro geochemistry of selected ground water samples in the wetland system in order to understand the salinity problem. A total of twenty-four ground water samples were collected from the basin for physico-chemical analysis during period November 2022-2023. Figure 1 shows the sampling locations in the map. The details of the sampling stations are indicated in Table 1.

Table 1: Details of the Sampling stations

Name of panchayath/municipality	Number of samples	Sampling code
Munniyoor	4	KDG1- KDG5
Koottilangadi	5	KDG6- KDG10
Vallikkunnu	5	KDG11- KDG15
Kadalundy	5	KDG16- KDG19
Thirurangadi	5	KDG20- KDG24

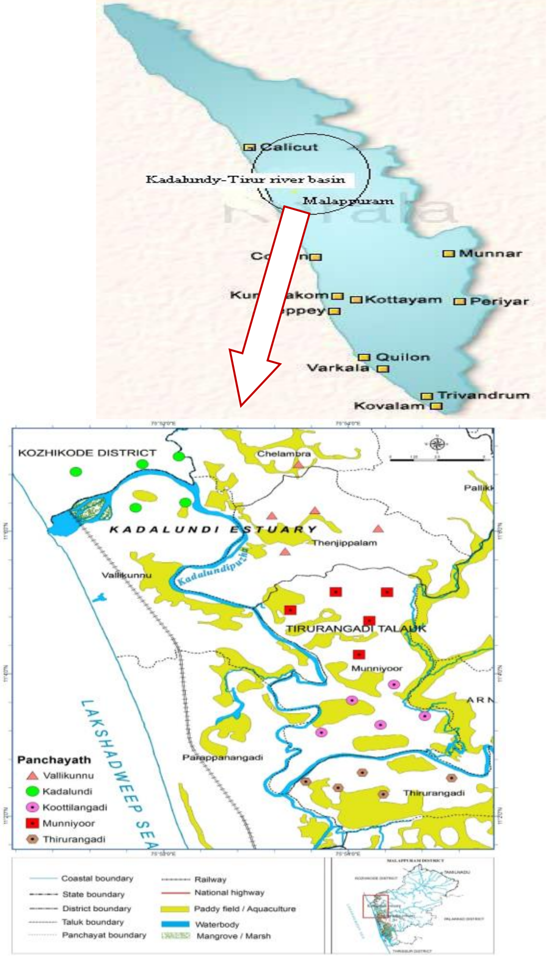


Figure 1: Map of the study area and sampling locations in Kadalundi River basin

Sampling and water quality analysis

. General procedures for groundwater sampling, preservation and chemical analysis were carried out according to standard procedures described by American Public Health Association, APHA (APHA, 1995). The locations were selected based on the available ground water and were representative of the whole reserve. At least three observations were recorded per location. The studied parameters are shown in Table 2 &3. An on-site water quality analysis was conducted in the field using a digital multiparameter to measure the temperature, pH, turbidity, and electrical conductivity (EC) at various locations in the studied river basin. and other chemical constituents were analyzed in the laboratory. Turbidity was measured using Nephelo turbidity meter Alkalinity, chloride, total hardness, calcium was analyzed titrimetrically. Sodium and potassium were analyzed by using flame photometer.

Statistical Analysis

Several statistical techniques were utilized to assess the water quality. In particular, a Pearson correlation analysis was performed to examine the associations among all pairs of the evaluated parameters. The possible hydro geochemical processes occurred in the groundwater was assessed from the Piper diagram and Durov's plots. Durov diagram for the major cation and anions plotted by SYSTAT software. Pearson's correlation matrix and Piper diagram were ploted using AQUACHEM software.

Results and Discussion

The concentration of cations, anions and other physico-chemical parameters analysed for the collected well water samples are shown in Table 2 & 3.

Ground water quality analysis

The pH value of water is an important indication of its quality and it is dependent on the carbon dioxide-carbonate-bicarbonate equilibrium. The pH values are within the permissible limit prescribed by WHO, ICMR and BIS. The result of the present study shows clearly the dominance of bicarbonate and it ranges between pH 7.10 and 8.10. The carbonate ion is dominant when pH is above 8.0. However, carbonate in most of the samples is absent. The EC is a useful parameter of water quality for indicating salinity hazards. In the present study area, the EC values widely varies between 270 µmhos/cm and 6920 µmhos/cm at 25°C. As per the standards prescribed by WHO, the maximum limit of EC is 1400 µmhos/cm. It is observed that waters of high EC values are predominant with sodium and chloride ions. The TDS value varies between 175 mg/l and 4490 mg/l. Waters can be classified based on the concentration of TDS (Wilcox 1955) [16] as given below:

The pH value of water is an important indication of its quality and it is dependent on the carbon dioxide-carbonate-bicarbonate equilibrium. The result of the present study shows clearly the dominance of bicarbonate and it ranges between pH 4.62 and 7.21. The carbonate ion is dominant when pH is above 8.0. However, carbonate in most of the samples is absent. The EC is a useful parameter of water quality for indicating salinity hazards. In the present study area, the EC values widely varies between 604 µmhos/cm and 7180 µmhos/cm at 25°C. As per the standards prescribed by WHO, the maximum limit of EC is 1400 µmhos/cm. It is observed that waters of high EC values are predominant with sodium and chloride ions. The TDS value varies between 386 mg/l and 4595 mg/l. In the present study chloride concentration varies from 108 to 1080 mg/l. The comparatively high chloride ion concentration was observed for the well water samples collected from the Kadalundi estuarine region. Calcium, chloride and total alkalinity in the water are inter-related. Calcium concentration varies from 32 to 840 mg/l.

Table 2. Major ion concentration of groundwater samples of Kadalundi river basin (KDG 1-12)

Parameters	**KDG1**	**KDG2**	**KDG3**	**KDG4**	**KDG5**	**KDG6**	**KDG7**	**KDG8**	**KDG9**	**KDG10**	**KDG11**	**KDG 12**
Temperature (0 c)	26.50	26.70	25.30	23.50	26.40	25.70	24.40	24.70	26.20	26.30	24.40	24.40
pH	5.12	4.91	4.62	6.28	4.91	6.28	4.50	6.70	4.91	5.90	6.80	6.80
EC (micro siemens/cm)	1560.00	780.00	764.00	1560.00	604.00	1578.00	620.00	1560.00	800.00	1580.00	2350.00	2340.00
Colour (Hazen)	4.40	1.30	0.56	18.40	1.30	18.40	1.20	18.40	1.30	18.40	4.50	22.40
Turbidity (NTU)	2.70	0.70	0.70	11.00	0.70	11.00	5.40	11.00	0.70	11.00	2.30	5.50
TDS (mg/l)	998.40	499.20	488.96	998.40	386.56	1009.92	396.80	998.40	512.00	1011.20	1504.00	1497.60
Total alkalinity	520.00	228.00	246.00	196.00	154.00	468.00	112.00	196.00	236.00	496.00	660.00	636.00
Chloride (mg/l)	220.00	116.00	96.00	400.00	84.00	144.00	56.00	400.00	120.00	360.00	220.00	232.00
Calcium(mg/l)	110.00	64.00	48.00	200.00	48.00	80.00	32.00	200.00	60.00	184.00	176.00	120.00
Sodium (mg/I)	46.00	16.00	24.00	86.00	36.00	78.00	16.00	78.00	52.00	56.00	102.00	56.-00

Table 3. Major ion concentration of groundwater samples of Kadalundi river basin (KDG13-24)

Parameters	**KDG13**	**KDG14**	**KDG15**	**KDG16**	**KDG17**	**KDG18**	**KDG19**	**KDG20**	**KDG21**	**KDG22**	**KDG23**	**KDG24**
Temperature (0 c)	24.60	24.70	25.70	25.80	24.00	24.20	24.20	24.00	26.20	26.30	26.10	26.60
pH	7.40	7.20	6.80	7.21	7.80	6.60	7.50	7.40	6.70	6.24	6.03	5.80
EC (micro siemens/cm)	2300.00	2270.00	2340.00	7180.00	6520.00	5860.00	5410.00	6320.00	5100.00	3500.00	236.000	2720.00
Colour (Hazen)	1.80	7.70	22.40	16.50	16.50	4.20	11.00	16.50	14.60	12.20	3.20	6.60
Turbidity (NTU)	5.40	7.90	15.50	9.60	9.60	2.40	8.00	9.60	8.50	6.40	2.30	4.10
TDS, (mg/l)	1472.00	1452.80	1497.60	4595.20	4172.80	3750.40	3462.40	4044.80	3264.00	2240.00	1510.40	1740.80
Total alkalinity	640.00	620.2	636.00	908.00	108.00	1600.00	108.00	1080.00	1040.00	136.00	660.00	634.00
Chloride (mg/l)	400.00	240.00	232.00	2400.00	1120.00	800.00	360.00	920.00	1200.00	360.00	284.00	368.00
Calcium(mg/l)	280.00	110.00	120.00	320.00	600.00	300.00	240.00	600.00	840.00	200.00	164.00	232.00
Sodium (mg/I)	156.80	450.50	324.00	1354.40	1254.40	744.00	288.00	1254.4	840.00	1600.00	386.00	476.00

From the analysed ground water quality parameters, the evaluation of hydrogeochemical processes and possibility of sea water intrusion in to the ground water systems in Kadalundi river basin was carried out by statistical analysis.

It is usually known that the hydro geochemical composition of coastal groundwater is affected by sea water intrusion, which is mainly controlled by cation exchange reaction rather than simple mixing processes (Appello,2005). On the other hand, hydro geochemical composition of fresh ground water was unaffected by sea water intrusion, which is dominated by calcium and bicarbonate ions. In seawater sodium and chloride are dominant ions. As a result, the adsorbed cation on the sediments in contact with sea water should consist dominantly of Na^{+}.

$$Na^{+}+1/2\ Ca\text{-}X_2 \longrightarrow Na\text{-}X+1/2\ Ca\text{-}X_2$$

When Ca^{2+} is exchanged with Na^{+}, the water becomes saturated for calcite and precipitation results. At high pH, Ca^{2+} and Mg^{2+} are usually transferred in to a solid phase; therefore, their concentrations are controlled by mineral precipitation (Lee, 2001)

Identification of major groundwater facies & hydrogeochemical evolution path in the ground water *system using piper diagram*

Piper plot of major chemical compositions of the groundwaters and the seawater is shown in Figure 2. If groundwater is simply mixed with sea water, the groundwater composition should be plotted on a straight line connecting the background fresh water and the sea water on the diamond shape field of piper diagram. From the plot, three principle groundwater facies are identified, which are Ca (Mg^{+}) Cl (+SO_4), Na-Cl, HCO_3^- types. Monitoring wells showing Na-Cl types of waters are most proximal to the coast. Major chemical composition of this type of groundwater is most similar to that of seawater, which strongly indicated that the groundwaters were evidently affected by the very saline water (Pulido-Leboeuf, 2004). Most samples belong to Na-Cl type. Substantial proportions of the ground waters showed a transition or mixed type behavior. From the lower two triangles of the piper plot, it was inferred that the ground water salinization occurred via cation exchange reaction and mixing between two end members (fresh or less affected ground water and sea water). One sample from Koottilangadi belongs to CaCl type. It is considered that the abnormal high concentration of calcium than that in the NaCl type water cannot be explained by the cation exchange reactions due to saline water intrusion in this well, agricultural and livestock activities may act as point contaminant sources (Sung-Wook Jeen et al. 2001)

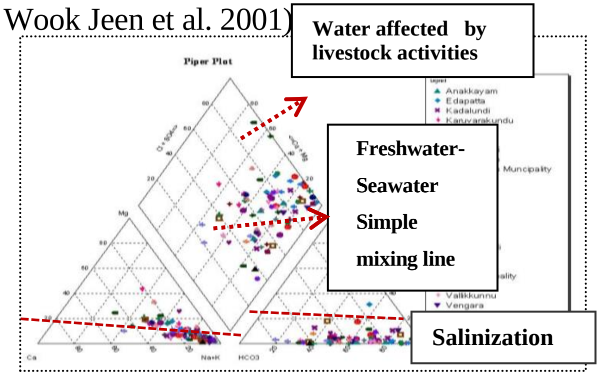


Figure 2 Piper diagram and hydrogeochemical evolution path in the ground water samples

Durov diagram is based on the percentage of the major ions in meq /L. Both the positive and the negative ion percentage total is 100%. The values of the cations and the anions are plotted in the appropriate triangular and projected in to the square of the main field. The advantage of this diagram is that it displays some possible geochemical processes that could affect the water genesis. Durov diagram for the major cation and anions plotted by SYSTAT software is illustrated in the Figure 3. The fields and the lines on the diagram show the classifications of the Lloyd and Heathcoat (1985).

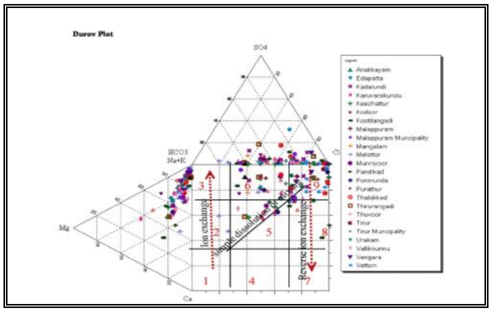


Figure 3 Durov diagram for the major cations and anions in ground water samples

From the Durov plot, two samples from Melattoor lies under field (2). It indicates that this water type is dominated by Ca and HCO_3 ions. Four samples from Vallikkunnu panchayath, one from Munniyur and one from Thirurangadi lies in field (5) it reveals that there is no dominant anion or cation, which indicates that the sample exhibits simple dissolution or mixing. One sample from Koottilangadi,Thuvoor and Pandikkad belongs to field (7), shows chloride and sodium dominant and the water may results from reverse ion-exchange of NaCl waters. Most of the samples lies under fields (6) and (9), i.e. field (6) is sulphate and sodium dominant water type that is not frequently encountered and indicates probable mixing influences and field (9) was chloride and sodium dominant frequently indicates end point waters ((Abdulaziz , 1998) .

Investigation of the possibility of sea water intrusion into the studied ground water system

Using Pearson's Correlation matrix

. The data were statically computed using correlation coefficient in order to indicate the sufficiency of one variable to predict other (Davis, 1986).

The results of the Pearson's correlation analysis are considered in the subsequent interpretation. A high correlation coefficient (near 1or -1) means a good relationship between two variables, and a correlation coefficient around zero means no relationship. Positive values of r indicate a positive relationship while negative values indicate an inverse relationship. The correlation coefficients of the studied parameters were shown in Table 4.

The positive correlation between $Ca^{2+}$and Mg^{2+} (0.802) is attributed to the precipitation of aragonite, dolomite and calcite. Precipitation takes place during cation exchange process which is the latter effect from seawater intrusion in to the ground waters. The lower concentration of Ca^{2+} compared to Na^{+}, is a result from the cation exchange processes that occurs naturally when sea water intrudes in to the ground water. Potassium shows positive correlation with all the analyzed parameters except $HCO_3^{-.}$ Such correlation is interpreted as arising from the interaction of ground water with coastal sediment which is derived from sea water intrusion in the area (Al-Agha,2004). The positive and significance correlation of K^{+} with both Cl^{-} and SO_4^{2-} which are generally very high in the sea may be in the light sea water intrusion as well. The correlation between Na^{+} and Cl^{-} shows around 0.626 which is interpreted as a result of seawater intrusion. The NaCl correlation shows the influences of seawater and sea water mixing. According to Mandel & Shiftan (1981), the average of Na-Cl signature (0.66) is less than that of sea water (0.87). In the study, Na-Cl signature is around 0.626 which is not as clear as theoretical correlation. This is simply meaning that sea water is over diluted by the ground water as a result of infiltration. In the studied samples two sets of strong relationship exist between major cation and anions.

1. Highly competitive relationship between ions with same charge but different valence number such as K^{+} with Mg^{2+} and SO_4^{2-} with $Cl^{-.}$
2. The affinity between ions having different charges but the same valence number, such as Cl^{-} and K^{+}.

The variation of this relationship may indicate the complexity of hydro geochemical components of the ground water. In general, two main factors can be considered that play a very important role in shaping the chemistry and quality of the ground water in these areas. These include anthropogenic and natural factors (sea water intrusion).

Table 4 Pearson correlation matrix for the ground water quality parameters

	E.C	HCO_3^-	TDS	Ca	Mg	Na	K	Cl^-	NO_3^-	SO_4^{2-}
E. C	1	0.099	1	0.609	0.931	0.836	0.251	0.94	0.72	0.532
HCO_3^-		1	0.967	0.714	0.485	0.055	-0.01	0.413	0.72	0.213
TDS			1	0.646	0.932	0.632	0.654	0.987	0.68	0.165
Ca				1	0.802	0.088	0.578	0.871	0.71	0.031
Mg					1	0.164	0.426	0.544	0.43	0.123
Na						1	0.965	0.626	-0.02	0.656
K							1	0.673	0.36	0.856
Cl-								1	0.39	0.916
NO_3^-									1	0.013
SO_4^{2-}										1

Using the Classification of groundwater samples

Groundwater of the study area can be classified based on the hydro geochemical characteristics as shown in the Figure. 4 and Table 5. Eight types of groundwater are recognized in the study area. Most of the groundwater samples, particularly near the coastal area belong to Na-Cl type. Groundwater of the $NaHCO_3$ type was negligible in the study area (1%). This implies that high salinity in the study area is mainly caused by recent sea water intrusion because the Na HCO_3 type water represents the partly flushed which remains of an anciently entrapped saline water body (Mercado 1985).

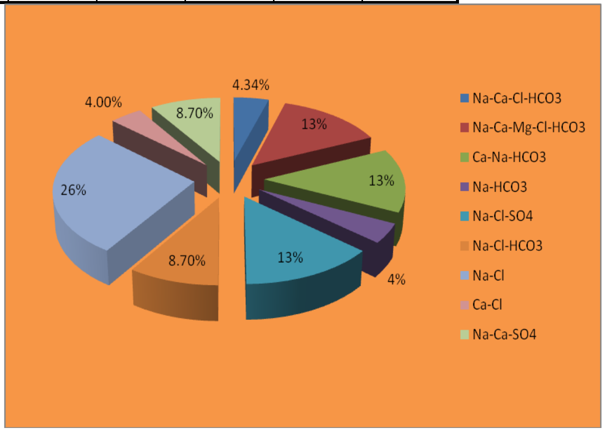
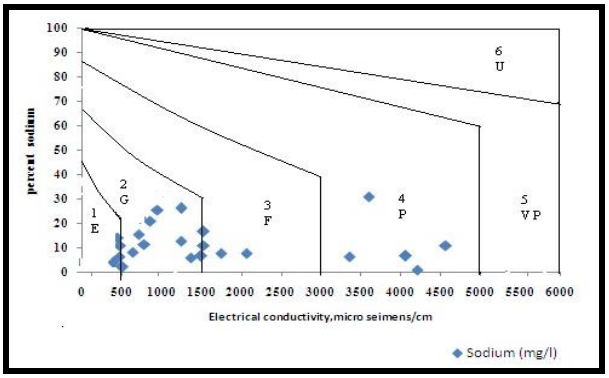


Figure 4. Classification of types of ground water samples of Kadalundi river

From the interpretation of irrigational water quality

Wilcox classified groundwater for irrigation purposes based on per cent sodium and electrical conductivity for the groundwater samples of Kadalundy - Tirur river basin. Wilcox diagram (Figure 5) was plotted by calculating sodium percentage and drawn against electrical conductance as shown below,



Note: E-Excellent, G-Good, F-Fair, P-Poor, VP-Very Poor, U-Unsuitable

Figure 5. Wilcox diagram for classification of groundwater samples of Kadalundi river basin.

Class1.Excellent: The total soluble salt content and sodium percentage of these waters are low enough that no problems should result from its use. From the diagram, 72% of the well water samples are found to be excellent.

Class2.Good: This water is suitable for use on most crops under most conditions. Extensive use of class2 water on clay soils were no leaching occurs may eventually cause the saline or sodic soil problems. In the present study 20% of groundwater samples belong to this class.

Class3.Fair: This water can be successively used for majority crops if care is taken to prevent accumulation of soluble salts including sodium, in the soil. Class 3 water samples can be used with little danger on permeable, well- drained soils. From the diagram, 2.6% of the well water samples are found to be fair.

Class4. Poor: Use of this type of water is restricted to well-drained permeable soils for production of salt tolerant crops. Use of this water on medium texture soils may cause soil salinity problems. This water is not recommended for use on fine texture soils. In the present study, only 6.6% of ground water samples belong to this class. i.e. all the samples from Vallikunnu & one sample from Koottilangadi.

Conclusion

The objective of the present study has been fulfilled in terms of applying different hydrochemical techniques to classify the hydrochemical facies prevailing in the ground water samples and to predict the hydrochemical processes taking place in the ground water matrix. Piper diagram, Durov plot, statistical analysis was used to achieve these objectives, these techniques are proved to be simple, useful and efficient. The ground water hydrogeochemical facies were classified into three distinct types: Na –Ca -Cl-HCO_3, Na-Cl and, Na-Cl- HCO_3 types. The increased Na occurs as a result of ion exchange reactions. From Piper plots, NaCl type is the main hydrochemical facies for ground water. Evidence suggests that, the occurrence of several hydrogeochemical processes, such as mixing, ion exchange and simple dissolution in the ground water system in Kadalundi-Tirur river basin. Wilcox diagram also reveals that a considerable percentage of ground water samples were saline and hence cannot be used for irrigational purposes.

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