Study on the nature of the evaluation of hydrogeochemical parameters in stratified aquifers of the Pondicherry region –South East India

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Abstract: *Coastal areas in continents sustain important human activities. Water resources in layered aquifers illustrate most of the problems affecting in Pondicherry region. Pondicherry is one such Coastal region with varied geological set up ranging from Archean to Recent formations. Groundwater occurs in Alluvium, Lower Cuddalore, Upper Cuddalore and Cretaceous aquifers. Samples were collected in tube wells representing the specific aquifers. A total of 98 ground water samples were collected during Pre- Monsoon and Post-Monsoon seasons in Pondicherry region. 54 water samples were collected during Pre-Monsoon covering different aquifers viz., Alluvial aquifer; Upper Cuddalore Sandstone aquifer; Lower Cuddalore Sandstone aquifer and Cretaceous aquifer and similarly 44 water samples during the Post-Monsoon. The samples were analyzed for major cations, anions and dissolved organic carbon. Statistical analysis were also adopted to find out the variation of ions with respect to temperature, lithology and to identify the hidden relationship between them. Stable isotopes (δD and δO^{18}) were also analyzed for specific samples representing different aquifers formations. It is observed that EC is higher in the Alluvial aquifer and TDS is higher and exceeding the ISI standard limits for drinking water in all the aquifers of the study area. Few of the groundwater samples in the study area are unsuitable for domestic, irrigation and drinking purposes. Higher ionic concentrations were noted in the Pre Monsoon and the dilution effect was found during Post-Monsoon. The geochemical process of evaluation indicates that during Pre Monsoon, ion exchange process was predominant. The leaching of DOC can result in localized reducing zones that affect the movement of contaminants for tens to hundreds of feet down gradient. The analysis of these samples shows that higher concentration of DOC was noted in the Alluvial formation during both the seasons. The Alluvial aquifers shows pH governed dissolution along the coastal tracts and NO_3 association in certain regions indicating*

Keywords*: Lithology, Groundwater, Major ions, Isotopes and DOC*

1. Indroduction

The water quality plays a vital role in human health and welfare. Groundwater quality data give important clues to the geologic history of rocks and indications of groundwater recharge, movement and storage [1, 2]. The hydrochemistry is essential to determine the origin of chemical composition of groundwater [3]. The hydrology and geochemistry of waters have been further discussed in the classic works of [4]. Determination of physical, chemical and bacteriological quality of water is essential for assessing its suitability for various purposes like drinking, domestic, agricultural and industrial uses. [5]. Organic carbon concentrations are also significant in the groundwater quality which is varies both spatially and temporally. Natural organic carbon is mainly derived from decomposing vegetation and other organic matter in the soil zone. Microbial oxidation also increases the organic carbon [6]. The Statistical have also been employed in identification of relationships between variables [7]. The study area is predominantly an agricultural zone with dense agricultural activities and also located near the coastal region. The purpose of this study was to determine the seasonal variation and the significance of DOC in the groundwater chemistry in the study area

2. Study area

The Pondicherry region is located on the east coast of India; it is surrounded by northern latitudes 11º45'–12º03' and eastern longitudes 79 º 37'–79 º 53' (Fig. 1) with seven communes. Three

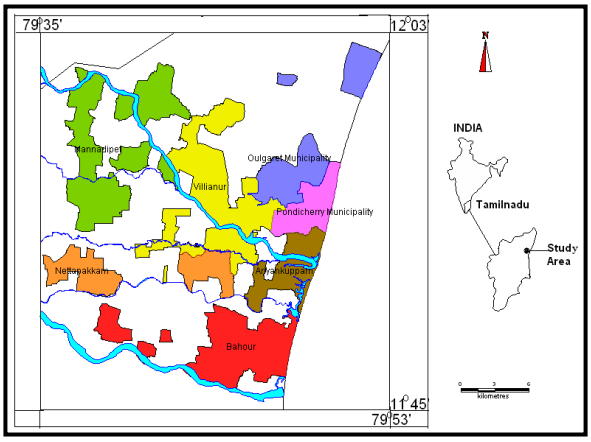

Figure 1: *Location map of the study area along with communes.*

major physiographic units are generally observed, namely (1) Coastal plain, (2) Alluvial plain and (3) Uplands. There are two major rivers draining the study area, namely the Gingee River in the north and Ponnaiyar River in the south. The subsurface lithology of the study area shows four geological period including Cretaceous, Palaeocene, Mio-Pliocene and Recent. The oldest sedimentary formation is of Cretaceous period. Four stratigraphic units were identified in this period [8] namely the Ramanathapuram, Vanur, Ottai and Turuvai formation. The Paleocene formation of Lower Tertiary is represented by the Kadapperikuppam and Manaveli formation. The Mio-Pliocene formation is represented by Cuddalore formation. The Recent (Quaternary) formation in the region is represented by alluvium.The variation and distribution of REE was studied by [9]

3. Methodology

Groundwater Samples were collected in tube wells representing the specific aquifers. A total of 98 ground water samples were collected during Pre-Monsoon (PRM-54) and Post-Monsoon seasons (POM-44) in Pondicherry region. covering different aquifers viz., Alluvial aquifer; Upper Cuddalore Sandstone aquifer; Lower Cuddalore Sandstone aquifer and Cretaceous aquifer and. Analysis of groundwater samples were carried in detail for different ions like HCO^{3-}, Cl^{-}, SO_4^{2-}, PO_4^{3-}, NO_3, H_4SiO_4, Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} using standard procedures [10,11]. Selected samples were analysed for Dissolved Organic Carbon (DOC) is analyzed as Non-purgable organic carbon (NPOC) by using the "Total Organic Carbon Analyser TOC-VCPN" (Shimadzu). Stable isotope of $\delta^{18}O$, δD isotope were analysed by using an Isotopic Ratio Mass Spectrometer (Finnigan Deltaplus XP).

4. Results and discussion

The Average value for the chemical composition of groundwater is given in Table 1. The range of EC during Pre monsoon ranges from 209µs/cm - 2360 µs/cm. and that of post monsoon range from 144µs/cm -1942 µs/cm. Higher EC is observed in the PRM in Alluvial Formation due to salt water intrusion [12].

Table 1: *Average values of the chemical composition of groundwater samples PRM and POM (all values are in mg/l except EC(µs/cm) and pH*

PRM	Alluvium	Upper Cuddalore	Lower Cuddalore	Cretaceous
pH	7.6	6.5	7.3	7.7
EC	1020	547.7	666.0	1109.2
Ca	40.5	28.9	30.5	50.8
Mg	28.8	6.7	21.0	29.3
Na	550.7	270.3	411.8	552.2
K	3.6	3.4	3.3	4.2
Cl	171.8	122.1	96.1	207.4
HCO_3	263.8	107.1	214.5	299.5
SO_4	7.1	5.4	5.5	8.3
PO_4	8.1	6.0	7.2	6.9
H_4SiO_4	118.0	113.9	145.5	93.0
TDS	829.2	428.6	511.6	950.3
NO_3	7.6	13.2	4.3	17.2
DOC	3.5	1.9	3.8	2.1
POM				
pH	7.1	6.9	7.1	7.2
EC	1494	704.4	582.3	1200.8
Ca	44.0	26.2	21.9	36.0
Mg	17.0	8.0	10.2	13.9
Na	216.7	185.4	144.8	149.7
K	16.4	16.0	16.7	15.6
Cl	215.9	198.9	132.4	143.8
HCO_3	379.3	222.3	206.6	310.4
SO_4	48.4	50.0	61.3	45.4
PO_4	0.3	0.4	0.4	0.4
H_4SiO_4	88.7	99.3	61.8	81.4
TDS	1045	493.1	407.6	840.6
NO_3	2.9	6.0	0.9	4.6
DOC	1.5	0.8	1.5	2.0

5. Hydrochemical facies:

Hydro geochemical facies interpretation is a useful tool for determining the flow pattern, origin of chemical histories of groundwater masses. Two major types of groundwater were identified by the piper facies, during pre-monsoon, Na-HCO_3 type and

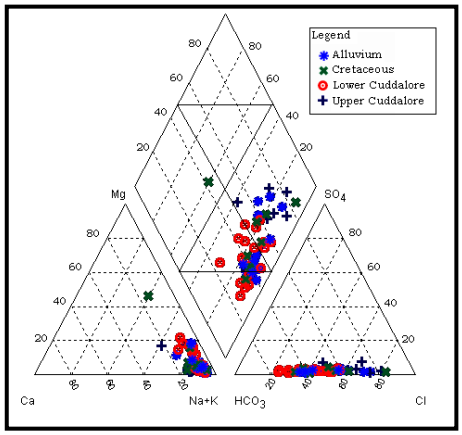

Figure 2. *Piper facies for groundwater collected during PRM*

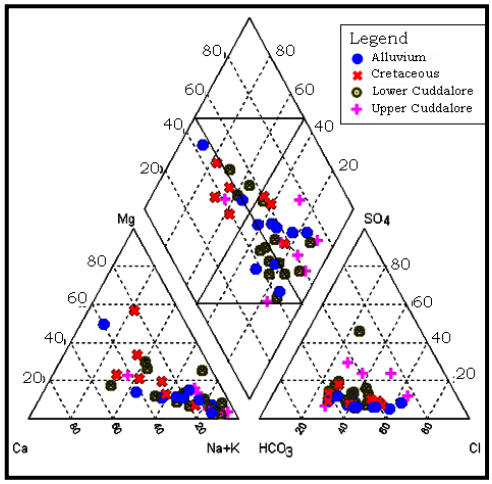

Figure 3. *Piper facies for groundwater collected during POM*

Na-Cl type indicating the saline nature in the groundwater [12] (Fig 2).All the Upper Cuddalore Sandstone aquifer samples were fall in the Na-Cl type along with few representations of Cretaceous and Alluvial aquifers. The Lower Cuddalore Sandstone aquifer samples along with majority of the Alluvial and Cretaceous aquifers samples fall in Na-HCO_3 facies. The dominant facies in all the aquifers is Na-Cl and Na-HCO_3 facies. During post-monsoon, few samples of Alluvial and Cretaceous aquifers fall in Ca-HCO_3 facies and that of Lower Cuddalore Sandstone in Ca-Cl facies (Fig 3). It's to be noted that there is a significant variation of cation in post-monsoon and variation of anion in pre-monsoon.

6. Hydrogeochemical Process Evaluation

A hydrochemical diagram proposed by [13] has been applied in this study to test if any of the interpreted hydrochemical processes can be identified by this method. The hydrochemical processes suggested are indicated in each of the four quadrants of the graph. These are broadly summarized as: Field 1 – Ca-HCO_3 type recharging waters; Field 2 – Ca-Mg-Cl type reverse ion-exchange waters; Field 3 – Na-Cl type end-member waters (sea water); Field 4 – Na-HCO_3 type base ion-exchange waters. The resultant diagram is exhibited in (Fig 4)

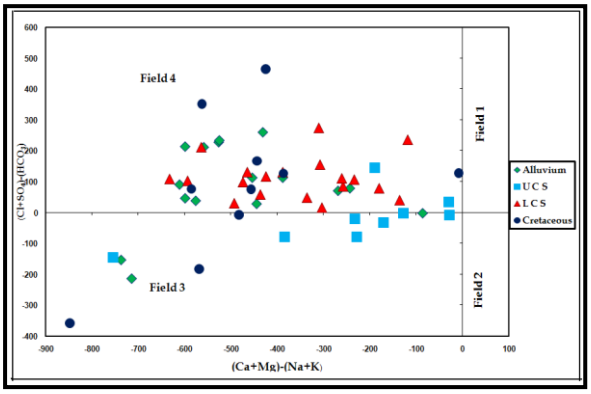

Figure4.*Chadda's Plot of Process evaluation for samples collected during PRM*

Almost all the samples of Upper cuddalore sand stone during PRM season (Fig 4) fall in the sea water mixing zone. There were good representations of Alluvial aquifer samples and few representations of Lower Cuddalore Sandstone and Cretaceous aquifers in this field (field 3). Majority of the Lower Cuddalore Sandstone, Alluvial and Cretaceous aquifers samples were noted in the cation exchange region (Field 4). The post-monsoon (Fig 5) also exhibits similar trend, but there is a reduction in the field 3 (sea water intrusion) and with representations of samples from Cretaceous aquifer, Alluvial and Lower Cuddalore Sandstone aquifers in the recharge region (Field 1).

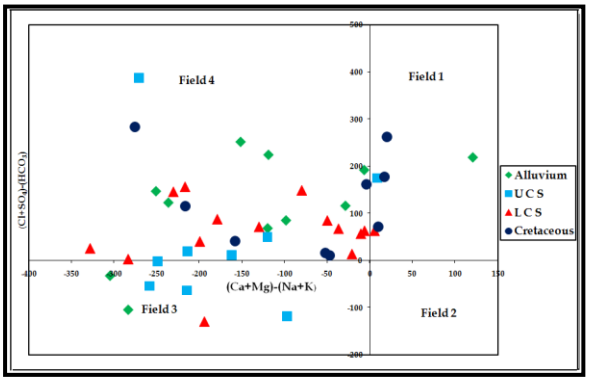

Figure 5. *Chadda's Plot of Process evaluation for samples collected during POM*

It is clear that field 3 and 4 are more common in both the seasons, of which more representation of the samples was in field 3. The impact of the monsoon is also noted by the samples in the field 1 in the post-monsoon.

7. Organic Carbon

The values of the organic carbon in groundwater shows that the Premonsoon samples have the higher range of DOC values .This may be due to the fact that the DOC is diluted during the Post monsoon. It is also noted that they are higher in Alluvium and lower Cuddalore aquifers. Alluvium contains the fine clay and Cuddalore sandstone composed of the peat and marcasite beds [14] DOC mobility is greatly related to pH [15].

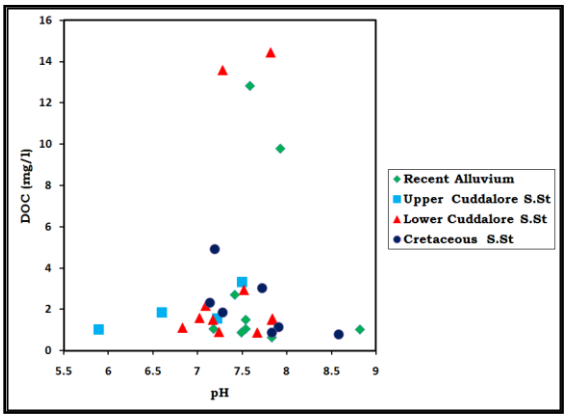

Figure 6. *Relationship between the pH and DOCfor the groundwater samples during PRM*

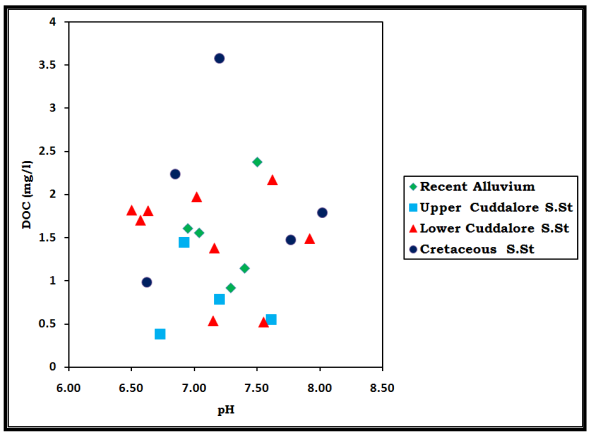

Figure 7. *Relationship between the pH and DOCfor the groundwater samples during POM*

The study area shows increasing DOC concentration with increasing pH in few samples of alluvium and Lower Cuddalore formation during PRM (Fig 6)because of higher salt concentrations in the alluvial aquifer and the direct infiltration of domestic sewage and industrial effluent [16]. But, samples from Upper Cuddalore and Cretaceous during PRM and POM(Fig 7) shows the low DOC with high pH values. The pH which generally increases the binding capability of humic substance [15, 17], hence the increase of binding capability results in the decrease of organic carbon release into the groundwater.

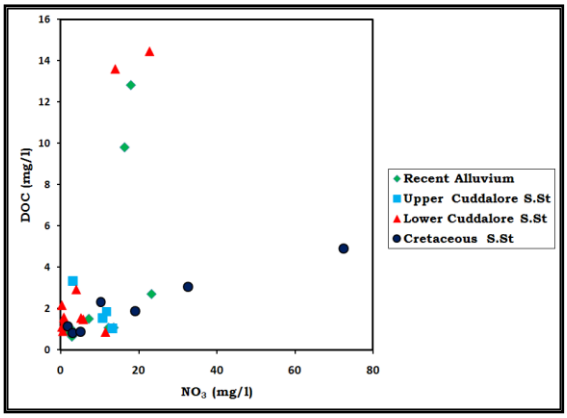

Figure 8. *Relationship between the NO_3 and DOC for the groundwater samples during PRM*

Dissolved organic Carbon is compared with the NO_3 to determine the source for DOC. Fig 8 shows increasing NO_3 with increasing the DOC in Cretaceous formation during PRM. Alluvium and Upper Cuddalore shows the higher DOC at lower nitrate concentration indicating the DOC is derived from the natural sources.

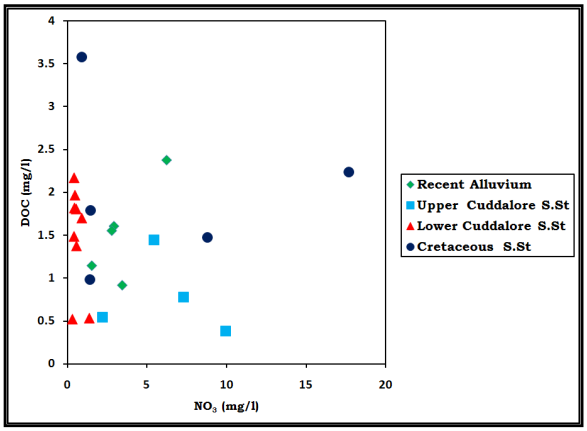

Figure 9. *Relationship between the NO_3 and DOC for the groundwater samples during POM*

The influence of NO_3 may also be due to anthropogenic sources such as Residential Water Softeners [18] and [19]. During POM the Alluvium and Cretaceous samples shows (Fig 9) a positive trend with DOC.

8. Isotope Studies

Inspite of the great complexity in different components of the hydrological cycle [20], $\delta^{18}O$ and δD in freshwaters correlate on a global scale. Craig's global meteoric water line (GMWL) defines the relationship between $\delta\ ^{18}O$ and δD in global precipitation as,

$$\delta D = 8\ \delta^{18}O + 10\ (‰\ SMOW)$$

Seven ground water samples were collected for isotope analysis. The samples from the Upper Cuddalore Sandstone and the Alluvial aquifers fall near the meteoritic water line and that of Alluvial aquifer falls very close to the LMWL.

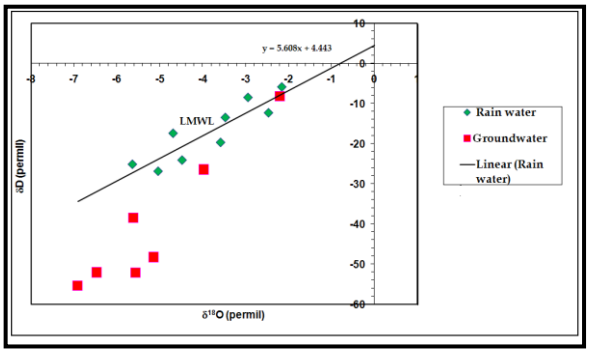

Figure 10.*Comparison of groundwater samples with LMWL*

It is also noted that the heavier isotopes are more in the Alluvial aquifer samples which may be due to the precipitation near the shore or that of saline intrusion [21].Samples of the Cretaceous and Lower Cuddalore Sandstone aquifers fall away from the meteoritic line (Fig 10) which may be due to the process of weathering of rocks/sediments or due to process of evaporation before recharge from other sources.

9. Statistical Analysis

The FA results for the groundwater samples in alluvial aquifer are shown in Table 3 and 4. Factor with Eigen values ≥ 1 emerged accounting for observed hydro chemical evolution in the study area.

During PRM Factor 1 is represented by Na, K and Cl (Table 3). This has a Total Data Variance (TDV) of 23.5%. The higher loading on Na+ of the factor seems to be related to three processes as anthropogenic sources, dissolution of Feldspars and sea water intrusion .The factor 2 represented by Na, Ca, HCO_3 with a TDV of 21% exhibits that predominate of Plagioclase Feldspar weathering.

Table 3. *Factor analysis for the PRM samples (Varimax rotated)*

	1	2	3	4
Na	0.67	0.56	-0.11	0.24
K	0.84	-0.23	0.11	0.00
Ca	0.34	0.73	0.19	0.15
Mg	0.13	0.35	0.45	0.43
Cl	0.87	0.36	0.09	0.07
HCO_3	0.12	0.87	-0.10	-0.01
H_4SiO_4	-0.08	0.14	-0.64	-0.16
PO_4	-0.06	0.37	0.33	0.05
SO_4	0.37	0.22	0.30	0.57
NO_3	0.15	0.16	0.81	-0.05
pH	0.23	0.33	-0.38	0.56

In POM Factor 1 is represented by Mg, Ca, Cl and HCO_3 with a Factor 3 represented by NO_3 with a TDV of the 13%, this factor also represented in the post-monsoon samples as third factor but with less TDV loading of Nitrate, This factor during both the seasons reveals that anthropogenic contamination plays significant role in the geochemical process of the study area.TDV of 19%. This factor exhibits the dominant of ion exchange process, Factor 2 is represented by silicate weathering (H_4SiO_4, Na, and HCO_3) with a TDV of 13%. This factor could be related to the breakdown in the rock dumps of minerals such as Feldspars due to weathering [22]. Factor 3 is represented by NO_3 with a TDV 11.9%. The NO_3 generally represents the influence of the anthropogenic activities.

Table 4. *Factor analysis for the POM samples (Varimax rotated)*

	1	2	3	4	5
Mg	0.58	-0.07	0.45	-0.08	-0.26
Ca	0.91	0.01	0.13	0.06	-0.13
K	-0.01	0.19	0.19	0.71	-0.14
Na	-0.01	0.56	-0.21	-0.15	0.69
Cl	0.70	0.20	0.02	0.05	0.20
HCO_3	0.79	0.59	-0.20	0.08	0.05
PO_4	-0.01	-0.21	0.01	-0.15	0.03
SO_4	-0.18	-0.13	0.20	0.41	0.56
H_4SiO_4	-0.09	0.70	-0.02	0.17	-0.53
NO_3	0.13	0.30	0.62	-0.07	-0.20
pH	0.06	0.06	-0.84	-0.08	-0.12

Factor 4 represented positive loading of K and negative loading of pH and Mg, representing ion exchange with a TDV of 10%. Factor 5 includes Na and SO_4 with a TDV 9.8%. This may be due to pollution or anthropogenic activities.

10. Conclusion:

The samples collected from different aquifers for two different seasons show that Electrical conductivity is higher in the Cretaceous and Alluvial aquifers .The PRM samples indicates the dominances of sea water intrusion. The Post-Monsoon samples exhibit dilution effect along with recharge apart from the ion exchange process. DOC in cretaceous are by the anthropogenic processes and that of .Cuddalore sand stone are derived from the lignite beds and microbial influences. In Alluvium DOC are derived from the anthropogenic and fine clay sediments .The stable isotopes show a suspect of recent sea water intrusion along the alluvium and the Upper Cuddalore aquifer.

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