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Hydrogeochemical characterisation of groundwater along the alluvial and lateritic zones of Northern Kerala, India

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ABSTRACT

Groundwater is one of the most valuable natural resources, playing a fundamental role in human health and wellness, socio-economic development, and ecosystem functioning. The aim of this study is to characterize the hydrogeochemical features of groundwater and determine the governing processes in the aquifers of alluvial and lateritic zones of Kasaragod district, Kerala. About 103 groundwater samples were collected from dug wells during pre-monsoon and post-monsoon from the study area. The EC values of the groundwater samples of alluvial zone varies from 50 to 3780 µS/cm during pre-monsoon and 30 to 5800 µS/cm during post-monsoon. In the lateritic zone, the range is 30 to 459 µS/cm during pre-monsoon and 26 to 423 µS/cm during post-monsoon. The Hill Piper diagram indicates dominance of Ca-Mg-HCO_3 water types in both alluvial and lateritic zone during pre-monsoon. Gibbs plot shows rock-water dominance in both aquifer zones suggesting that the interaction between the groundwater and aquifer material is controlling the groundwater chemistry. In factor analysis total variance had strong positive loading on EC, TDS, Na and Cl during pre-monsoon and Ca, Mg, HCO_3 during post-monsoon. The majority of the groundwater samples in both alluvial and lateritic aquifer zones in the study area falls in the suitable for drinking category and few samples which are exceeding the WHO and BIS water quality standards limits due to anthropogenic activities.

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1. INTRODUCTION

Water is the most important and non-replaceable natural resource on the planet, as water is required for the growth, survival, and wellness of all life forms. It is essential to human health, growth and overall functioning of ecosystem (Reyes-Toscano et al., 2020). Groundwater is the primary supply for drinking, residential, industrial, and cultivation purposes in India. Over one third of world's most significant groundwater sources have drained, while some of the most significant aquifers are under increasing stress (Richey et al., 2015). The extraction of groundwater has been increasing globally during the last decades

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due to increasing population per capita demand of urbanization and industrialisation (Aju et al., 2022). More than 2 billion people depend on groundwater for drinking purpose globally (Achu et al., 2020). The requirement for potable water is rapidly increasing in tandem with population growth, leading to water scarcity (Stavridis et al., 2017). The ground water pumping for agricultural purposes may have impact on the recharge pattern of the associated river basin (Yue et al., 2020). Groundwater pollution has become severe problems due to natural sources and human activities, which can result in poor drinking water quality and potential health problems (Szklarek et al., 2022; Arumugam et al., 2023). The suitability of water for each purpose depends on numerous chemical constituents dissolved in water (Swetha et al., 2021).

Groundwater quality is crucial because it affects the well-being and growth of society in terms of health, food production and economy (Khan et al., 2020; Trivedi et al., 2023). The variations in groundwater quality in a region are a consequence of physical and chemical characteristics that are highly impacted by lithology and anthropogenic factors (Gautam et al., 2022). The water quality would also guide us in accessing information about the regions wherein the water has travelled (Chidambaram et al., 2011). The composition of replenished water, seasonal rainfall, surface water, and subsurface hydrogeological processes significantly influence quality of ground water (Twarakavi and Kaluarachchi, 2006). The water chemistry can be altered by a number of variables such as mineral dissolution, the residence time of dissolved ions, the weathering of rock, and the nature of pollutants (Khan et al., 2021). In the studies of groundwater hydrogeochemical characterization, it is further influenced and controlled by cation exchange, evaporation, and rock-water interaction (Rajmohan and Elango, 2004; Wang et al., 2022).

In order to analyze the distribution of significant ion chemistry in the area, various geochemical processes in the aquifers should be determined (Raju et al., 2011). Studying the hydrochemistry and ionic interactions provides insights into the mechanisms that dictate solute chemistry and its origins (Ribinu et al., 2023). Ionic shifts in groundwater quality are caused by the interaction of rocks and water, and oxidation and reduction reactions take place when water percolates into aquifer (Krishnakumar et al., 2009; Brindha and Elango, 2012; Aher et al., 2022). India is the world's largest consumer of groundwater, using over 230 cubic kilometers of underground water per year (Lalitha et al., 2021). The challenge of water scarcity is rapidly outpacing other issues in urban India, with recent reports highlighting the projection that Indian cities will confront substantial water shortages by the year 2050 (Sahu and Debsarma, 2023). Despite receiving an annual rainfall of 3100 mm, Kerala is among the Indian states facing challenges with low per capita freshwater availability (Anoop et al., 2021). It does have the maximum number of open wells compared to any place in the world, although many of those wells do not provide enough water during summer season (Jesiamma, 2005).

Coastal regions face significant vulnerability to various hazards, emphasizing the necessity for effective strategies to mitigate coastal vulnerability (Gopinath et al., 2021; Vrinda and Mohammed-Aslam, 2021). Its coastal aquifers are struggling from quantity and quality concerns (Dhanya and Shaji, 2017; Jesiya et al., 2021). There are numerous studies carried on groundwater have been assessed by researchers in Kerala on hydrochemistry and groundwater quality (Laluraj et al., 2006; Manjusree et al., 2009; Vincy et al., 2015; Nandakumaran and Balakrishnan, 2020). Kasaragod has an excellent groundwater reserve due to laterite formations covering 70% of the district, which retains and percolates water more efficiently due to its porous characteristic. There are few researches focusing on the groundwater quality of lateritic aquifers in northern Kerala (Arjun et al., 2021; Anoop et al., 2021; Sarath et al., 2023; Mouvanal Haridas et al., 2023). Evaluation of hydrogeochemical characteristics is urgently needed in order to apply water resources management plans and remediation strategies (Li et al., 2014; Jiang et al., 2015; Swetha et al., 2022). The objective of the present study is to determine the spatio-temporal variation and to understand the hydrogeochemical aspects of groundwater of alluvium and lateritic zones of study area in coastal and inland zones of Kasaragod district.

2. STUDY AREA

The study encompasses an area of 758 km^2 within Kasaragod district, Kerala state. It is bordered to the north by Dakshina Kannada district of Karnataka State, to the south by Kannur District of Kerala, and to the west by the Lakshadweep Sea. The geographical coordinates of the study area range from $75^\circ\ 02'$

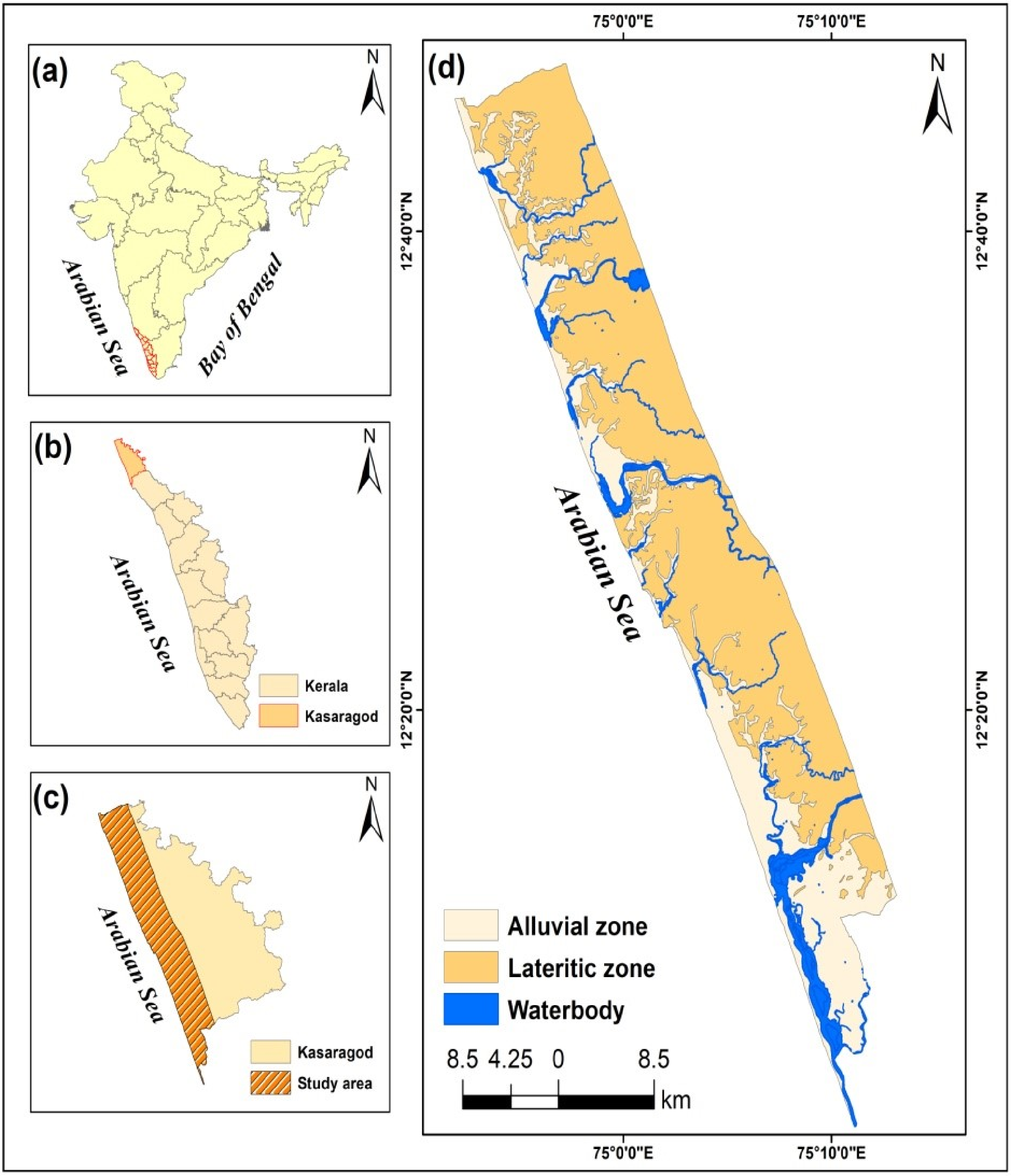

Fig. 1. Study area map of groundwater aquifer zones in Kasaragod district, Kerala.

4.17″ E to 75° 07′ 20.12″ E Longitude and 12° 02′ 35.59″ N to 12° 45′ 31.85″ N Latitude. Nine rivers traverse through the study area, with annual stream flow ranging from 307 to 4000 mm^3. The average monthly maximum temperature fluctuates between 29.2 °C to 33.4 °C, while the minimum temperature

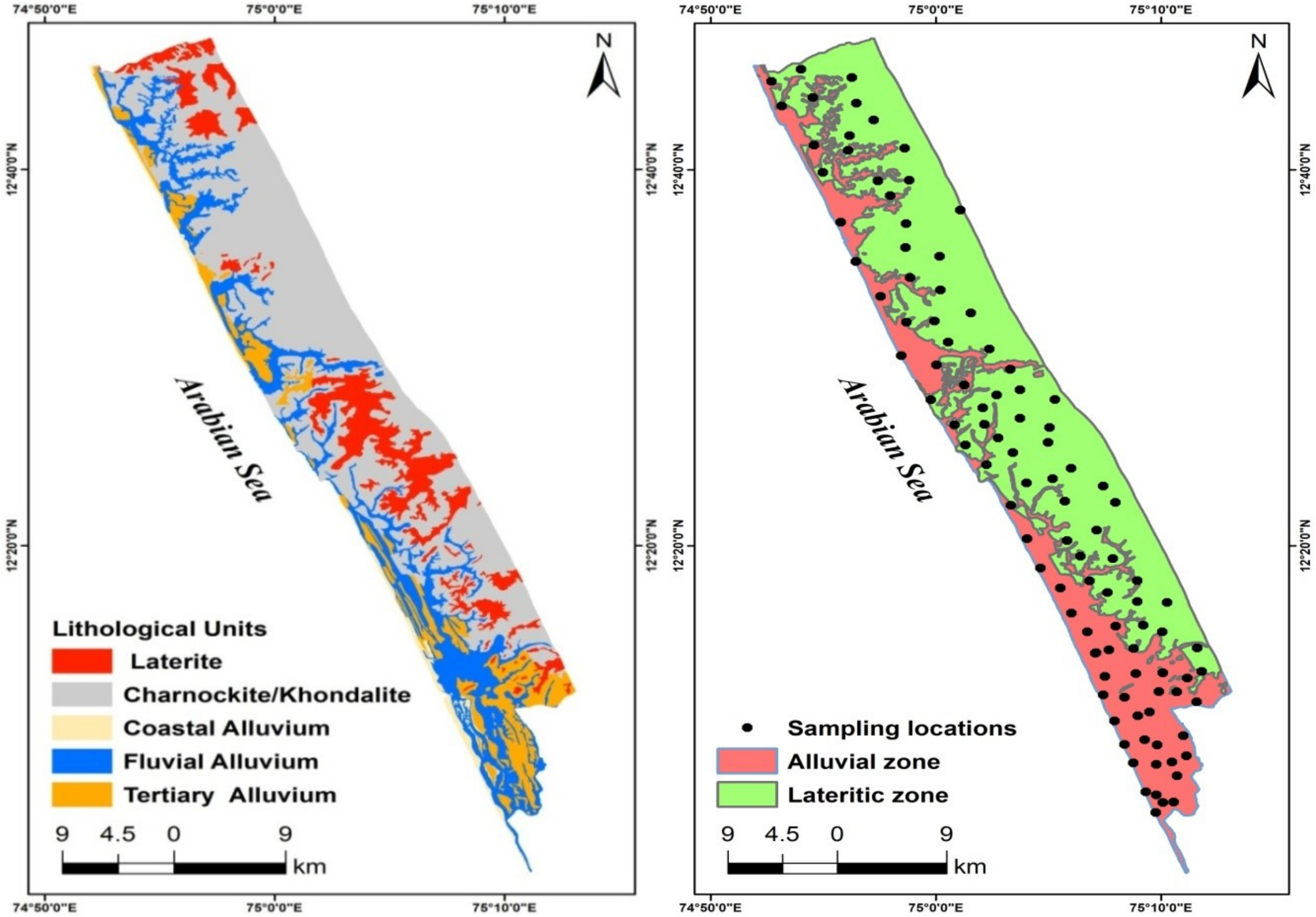

Fig. 2. Lithology map and groundwater sampling location map in study area.

ranges from 19.7 °C to 25 °C. The region experiences a humid tropical climate, with an average annual rainfall of approximately 3000 mm (CGWB, 2013).

2.1. Geological settings

Geologically, the Kasaragod area is predominantly composed of crystalline rocks and exhibits broad lateralization. From a physiographical perspective, the district can be categorized into three distinct units: Coastal plains, Midlands, and the Eastern highland region (Basak and Nizimuddin, 1985). The study area is divided into five geological formations, namely Coastal alluvium, Fluvial alluvium, Gneiss/Charnockite/Khondalite, Laterite, and Tertiary alluvium. It includes alluvial zone covering 254 km^2 and lateritic zones about 504 km^2. The Lateritic zone encompasses approximately 66% of the total study area. Coastal alluvium is found in narrow strips with increasing width to the south and reaching about 5 to 7 km around southern coast (District survey report, 2016). The Coastal plain is characterized by secondary soils that are sandy and sterile, with poor water-holding capacity (Arjun et al., 2021).

2.2. Methodology

The selection of sampling points was demarcated through a thorough field visit utilizing a handheld Garmin E-Trex 12-channel GPS device, GIS software, and SOI topographic maps (1:50,000). A comprehensive questionnaire for well inventory was devised to gather information pertinent to the present hydrogeological status of the study area. Physical parameters including temperature, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), and salinity were assessed using the Eutech multiparameter tester (PCS Testr 35). Hydrochemical analysis of groundwater samples from the coastal areas of Kasaragod district was conducted, involving 103 open wells during Pre-monsoon (April) and Post-monsoon (December) in 2017. In-situ measurements of pH, temperature, EC, TDS, and salinity were conducted using the Multi-Parameter meter kit (Eutech

PCTestr 35). The collected samples were preserved under specified conditions, and hydrochemical analyses were carried out in accordance with the standards set by the American Public Health Association (APHA, 2012).

3. RESULTS AND DISCUSSIONS

3.1. Physico- chemical parameters

The pH of the groundwater samples of alluvial zone varies from 5.1 to 8.6 and an average of 6.6 during pre-monsoon and 4.1 to 7.8 and an average of 6.1 during post-monsoon. In lateritic zone it varies from 5.4 to 8.6 and an average of 6.6 during pre-monsoon and 4.3 to 6.9 and an average of 5.3 during post-monsoon. The desirable limit of pH of water prescribed for drinking purpose (WHO, 2012) ranges from 6.5–8.5. Highest pH value of 8.6 was recorded in alluvial zone near to the coast. In alluvial zone, 63% of the samples meet the specified criteria during the pre-monsoon, while 32% comply during the post-monsoon period. In lateritic zone, 61% of samples fall within the established limits in the pre-monsoon, and only 7% meet the criteria during the post-monsoon period. Variations in hydrological conditions, land use, or geological features can all contribute to change in water quality between zones and seasons (Laonamsai et al., 2023). The slightly acidic nature of groundwater is a result of CO_2 addition through rainwater and the dissolution of carbon dioxide and organic acids, originating from the decay and subsequent leaching of plant materials (Langmuir, 1997). The predominance of lateritic soil could be linked to the notably more acidic characteristics of the groundwater compared to the alluvial aquifer (Laluraj et al., 2006). An additional factor that lowers pH is the use of acid producing fertilizers for agricultural activities (Akhil et al., 2013). The EC values of the groundwater samples of alluvial zone varies from 50 to 3780 µS/cm during pre-monsoon and 30 to 5800 µS/cm during post-monsoon. In lateritic zone it varies from 30 to 459 µS/cm during pre-monsoon and 26 to 423 µS/cm during post-monsoon. Majority of the samples reported conductivity below the acceptable limit of 1500 µS/cm implying low enrichment of salts during both seasons in lateritic zone. The EC value increases from the lateritic to the alluvial area in both seasons, with a comparatively higher EC value observed along the coastal area. The decrease in EC values from pre-monsoon to post-monsoon is attributed to the dilution of groundwater from rainfall (Gopinath, 2003; Rao et al., 2022). TDS in groundwater are mostly caused by the rainwater seeping through the unsaturated zones and dissolving salts that are present in the aquifer (Anoubam et al., 2017). This increase can be attributed to a combination of natural and human-induced activities (Patel et al., 2020).

3.2. Major ion chemistry in groundwater

The Sodium concentration of the groundwater samples of alluvial zone varies from 4.9 to 915 mg/l during pre-monsoon and 4.3 to 1020 mg/l during post-monsoon. In lateritic zone it varies from 2.9 to 41.7 mg/l during pre-monsoon and 3 to 40 mg/l during post-monsoon (Table 1). Higher concentration was recorded in alluvial zone compared to laterite zone (Fig. 5 a & b). All samples in lateritic zone exhibited sodium levels below the acceptable limit 200 mg/l (BIS, 2012). The occurrence of sodium in this investigation can be attributed to processes such as silicate weathering, mineral dissolution, and anthropogenic sources (Srinivasamoorthy et al., 2013). The Potassium concentration of the groundwater samples of alluvial zone varies from 0.4 to 52 mg/l during pre-monsoon and 0.1 to 25 mg/l during post-monsoon. In lateritic zone it varies from 0.3 to 5.9 mg/l during pre-monsoon and 0.4 to 18 mg/l during post-monsoon. All samples were below the acceptable limit 12 mg/l (WHO, 2012), during both the pre and post-monsoon seasons in lateritic zone.

Calcium concentration of the groundwater samples of alluvial zone varies from 1.2 to 85.2 mg/l during pre-monsoon and 1.9 to 136 mg/l during post-monsoon. In lateritic zone it varies from 1.6 to 22.4 mg/l during pre-monsoon and 2.3 to 30 mg/l during post-monsoon. All samples in lateritic zone are within the limits during both seasons. Calcium is crucial for the proper functioning of the nervous system, the heart, and blood clotting (Anoop et al., 2022). Magnesium concentration in alluvial zone, range varies from 0.2 to 61.9 mg/l during pre-monsoon and 0.4 to 64.6 mg/l during post-monsoon. In lateritic zone it varies from 0.2 to 27.6 mg/l during pre-monsoon and 0.4 to 17.7 mg/l during post-monsoon. In Lateritic zone all the samples are within BIS limits 30 mg/l during both the pre and post-monsoon. The source of magnesium in groundwater is decomposition of silicate magnesium minerals like olivine, pyroxene, amphiboles and biotite (Saha et al.,

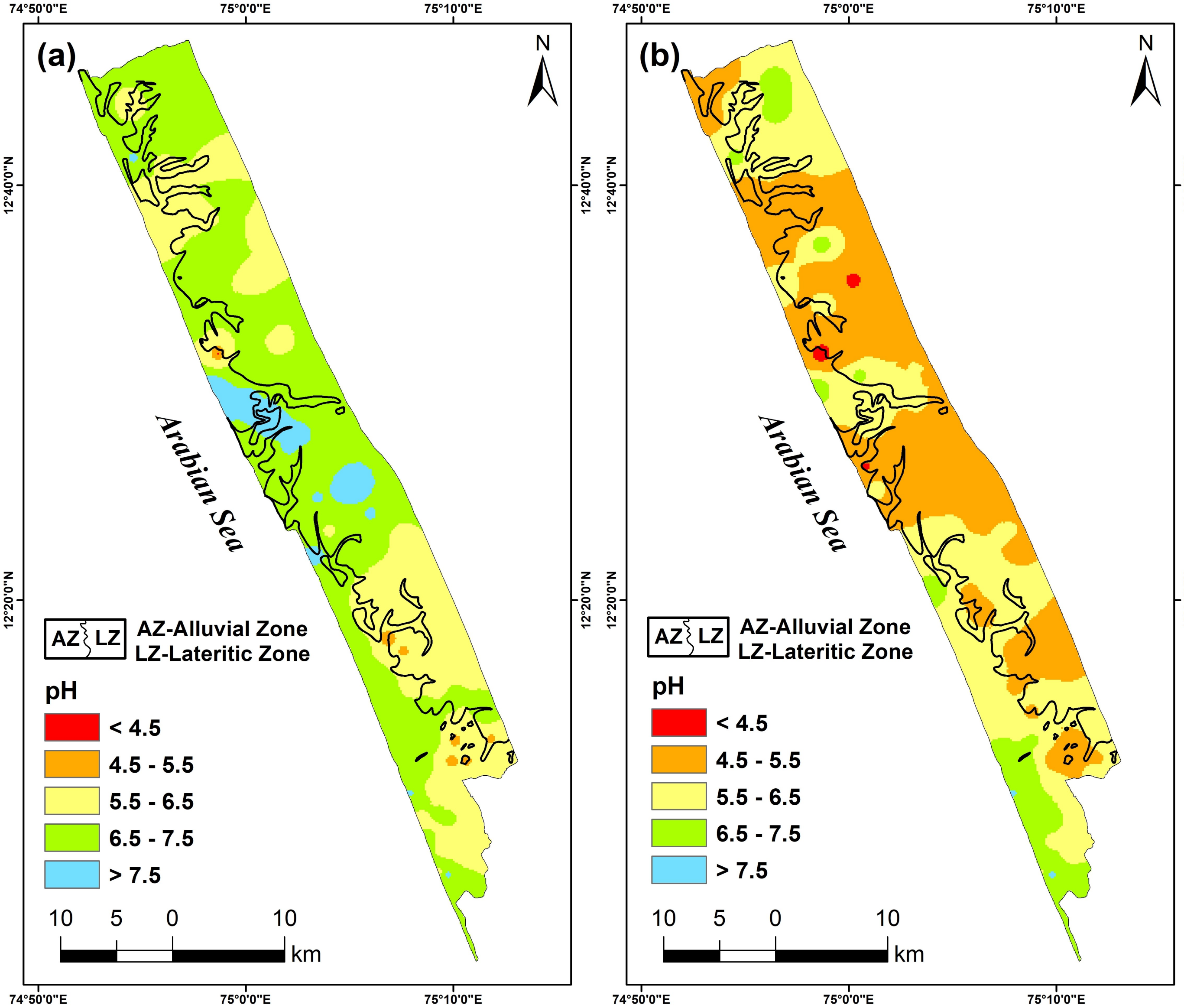

Fig. 3. (a & b) Spatial distribution of the pH in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

2019). The bicarbonate concentration of the groundwater samples of alluvial zone varies from 5.9 to 243 mg/l during pre-monsoon and 10.7 to 249 mg/l during post-monsoon. In lateritic zone it varies from 9.5 to 158 mg/l during pre-monsoon and 9.5 to 113 mg/l during post-monsoon. In the alluvial zone and lateritic zone all samples met the permissible limits during the pre-monsoon and post-monsoon seasons. Anthropogenic sources such as fertilizers, waste water from industries and cleaning reagents used in household also increase the bicarbonates in groundwater (Manasa and Mehta, 2020).

Sulphate concentration of the groundwater in alluvial zone varies from 0.3 to 264 mg/l during pre-monsoon and 0.7 to 331 mg/l during post-monsoon. In lateritic zone varies from 0.2 to 27.8 mg/l during pre-monsoon and 0.4 to 78.8 mg/l during post-monsoon. In Lateritic zone all the samples are within acceptable limits 200 mg/l (BIS, 2012) during both the pre and post-monsoon. Chloride in alluvial zone, ranges vary from 5.6 to 1052 mg/l during pre-monsoon and 7.8 to 1487 mg/l during post-monsoon. In lateritic zone varies from 3.8 to 46.4 mg/l during pre-monsoon and 5.6 to 37.5 mg/l during post-monsoon. In lateritic zone all the samples are within limits 250 mg/l during both the pre and post-monsoon. In the Chandragiri river basin, higher concentrations of these ions are observed. The seasonal variation in ionic parameters reveals a decrease in ionic concentration from pre to post-monsoon, in-

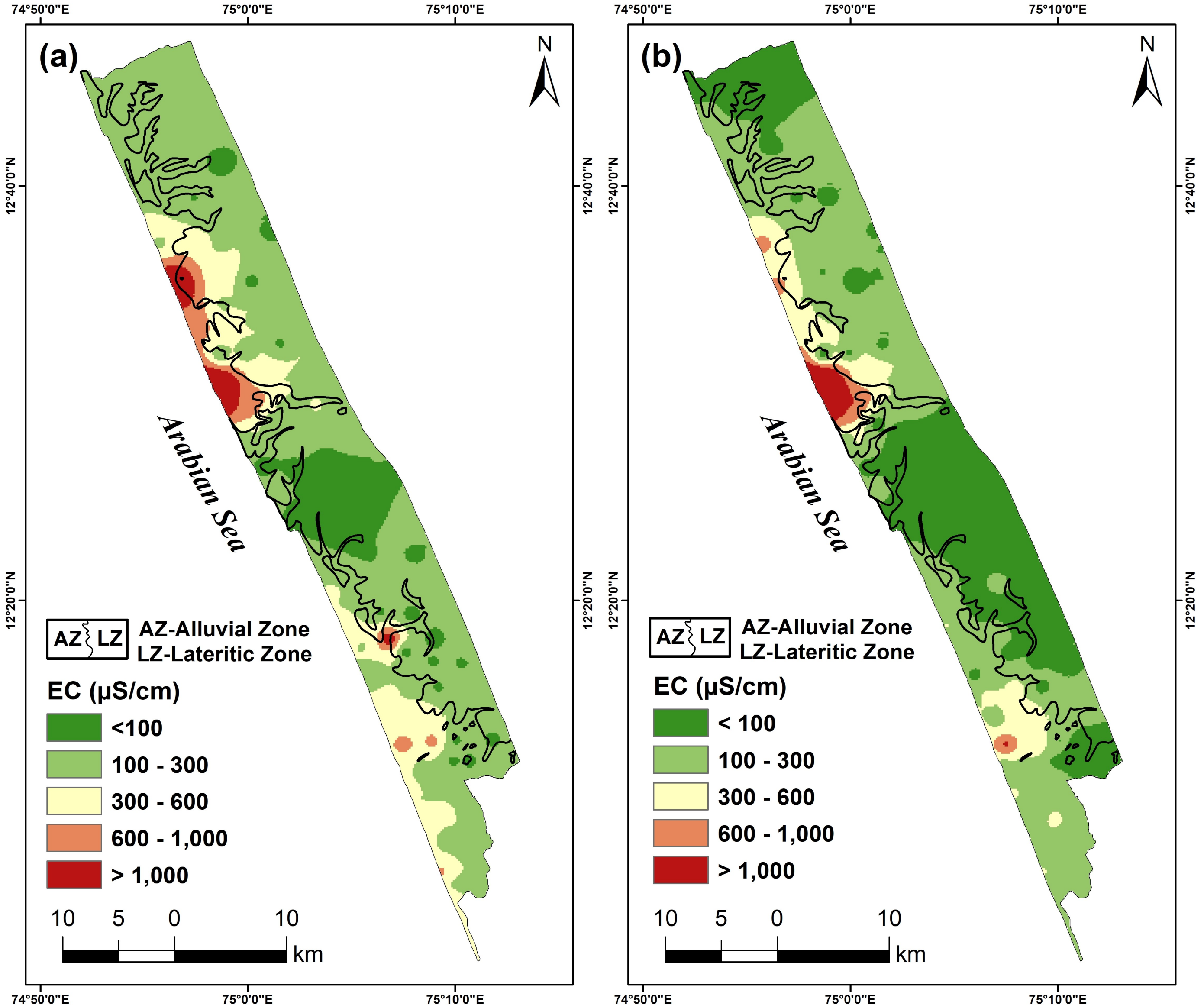

Fig. 4. (a & b) Spatial distribution of Electrical Conductivity in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

dicating enhanced dilution due to rainfall in the study area. The majority of samples fall within the limits set by WHO and BIS. The order of cation dominance is Na > Ca > Mg > K and, anion dominance is HCO_3 > Cl > SO_4 during pre and post-monsoon in both alluvial zone and lateritic zone.

3.3. Hydrogeochemical classification of groundwater

The hydrogeochemical origin of groundwater can be studied by displaying the major cations and anions concentration in the Piper diagram. It is a convenient method to classify and categorize the water type on the basis of dominant ion of the study area (Aghazadeh and Mogaddam, 2010). In alluvial zone, Ca-Mg-HCO_3 is dominant water type in both pre and post-monsoon (Fig. 9 a & b). During pre-monsoon:- Ca-Mg-HCO_3 > Na-K-Cl-SO_4 > Ca-Mg-Cl-SO_4 > Na-K-HCO_3. During post-monsoon:- Ca-Mg-HCO_3 > Na-K- Cl-SO_4 > Ca-Mg-Cl-SO_4. In lateritic zone, Ca-Mg-HCO_3 is dominant water type during pre-monsoon and Na-K-Cl-SO_4 during post-monsoon (Fig. 10 a & b). During pre-monsoon:- Ca-Mg-HCO_3 > Na-K-Cl-SO_4 > Na-K-HCO_3 > Ca-Mg-Cl-SO_4 and in Post-monsoon:- Na-K-Cl-SO_4 > Ca-Mg-HCO_3 > Ca-Mg-Cl-SO_4 > Na-K-HCO_3. About 67% samples in alluvial zone and 38% in lateritic zone were observed with no change in water type. In lateritic zone, groundwater exhibits a predominance of bicarbonate ions over sulfate and chloride ions, indicating its bicarbonate nature (Laluraj et al., 2006).

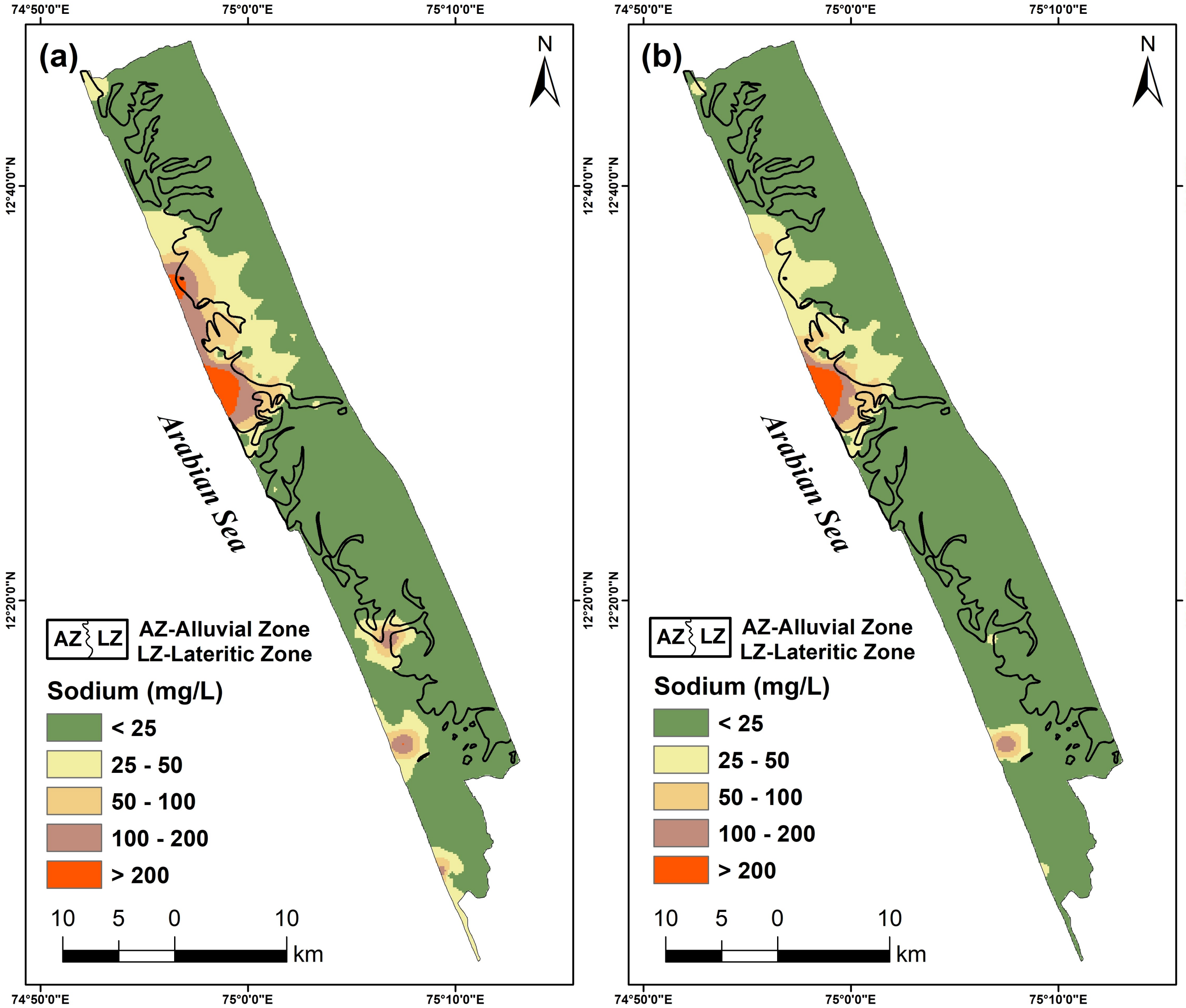

Fig. 5. (a & b) Spatial distribution of the sodium in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

Table 1. Physico-chemical parameters of groundwater in alluvial and lateritic zones during Pre and Post-monsoon.

Pre monsoon		**pH**	**EC µS/cm**	**TDS mg/l**	**Na^+ mg/l**	**K^+ mg/l**	**Ca^{2+} mg/l**	**Mg^{2+} mg/l**	**HCO_{3-} mg/l**	**So_4^{2-} mg/l**	**Cl^- mg/l**
Alluvial zone	Min.	5.1	50	33.5	4.9	0.48	1.2	0.24	5.9	0.3	5.6
	Max.	8.6	3780	2533	915	52	85.2	61.9	243	264	1052
	Avg.	6.6	432	289	53.5	6.3	23.2	6.0	65.3	25.7	67.7
Lateritic zone	Min.	5.4	30	20.1	2.95	0.3	1.6	0.2	9.5	0.2	3.8
	Max.	8.6	459	307	41.7	5.9	22.4	27.6	158	27.8	46.4
	Avg.	6.6	144	96.5	11.3	2.2	7.1	2.3	39.7	6.6	12.2
Post monsoon		**pH**	**EC µS/cm**	**TDS mg/l**	**Na^+ mg/l**	**K^+ mg/l**	**Ca^{2+} mg/l**	**Mg^{2+} mg/l**	**HCO_{3-} mg/l**	**So_4^{2-} mg/l**	**Cl^- mg/l**
Alluvial zone	Min.	4.1	30.9	24.7	4.3	0.1	1.9	0.4	10.7	0.7	7.8
	Max.	7.8	5800	4070	1020	25	136	64.6	249	331	1487
	Avg.	6.1	370	263	39.1	4.5	22.2	6.1	70.2	32	56.4
Lateritic zone	Min.	4.3	26.6	18.8	3.0	0.4	2.3	0.4	9.5	0.4	5.6
	Max.	6.9	423	299	40	18	30	17.7	113	78.8	37.5
	Avg.	5.3	93.0	66.2	9.9	2.0	6.6	2.2	28.3	7.67	13.4

The identification of various hydrochemical processes was carried out using Chadha's plot diagram (Chadha, 1999). The data was converted into milliequivalent percentages and expressed as the differ-

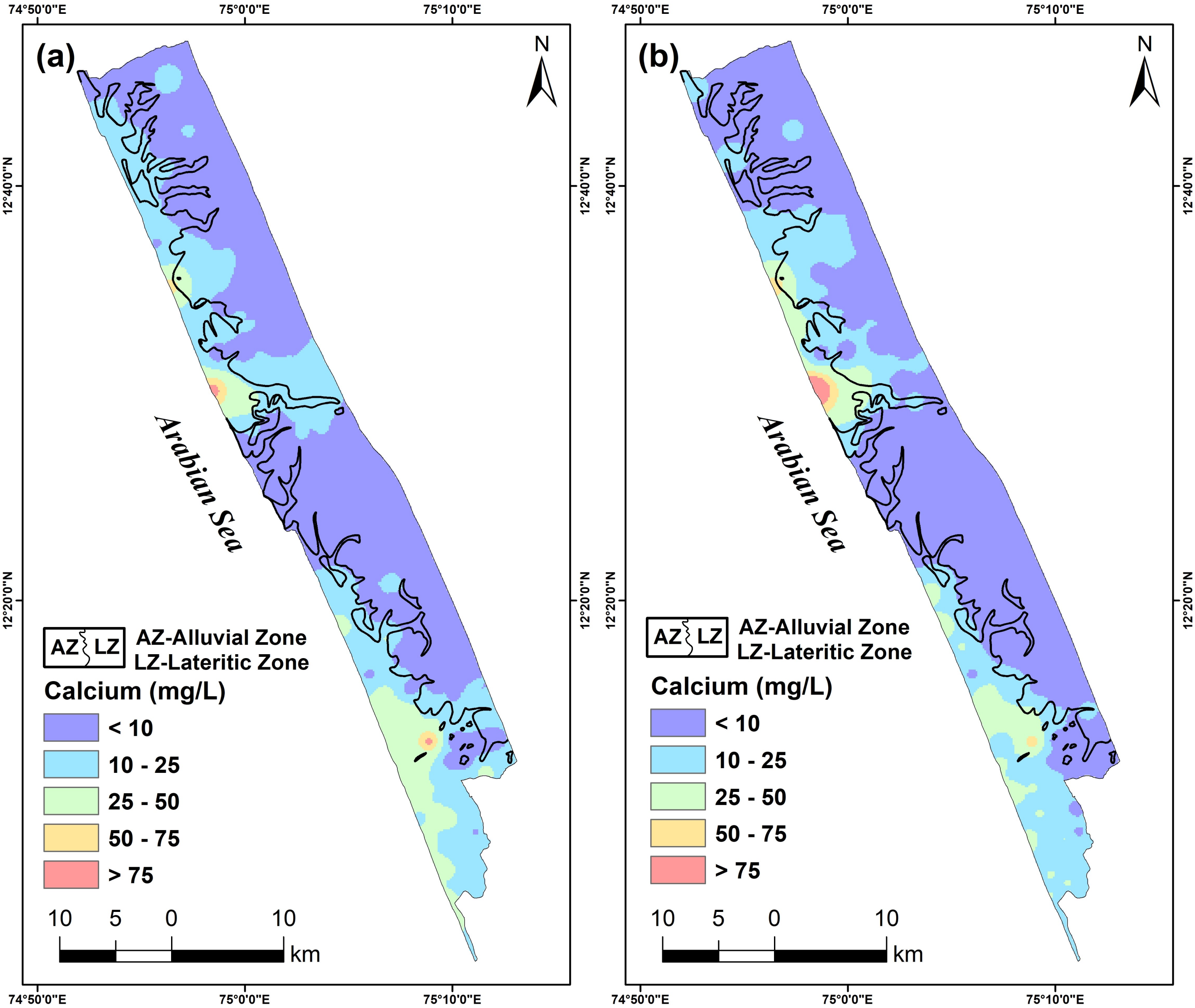

Fig. 6. (a & b) Spatial distribution of calcium in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

ence between alkaline earths (Ca + Mg) and alkali metals (Na + K) for cations, as well as the difference between weak acidic anions ($HCO_3 + CO_3$) and strong acidic anions ($Cl + SO_4$). In Chadha's plot are broadly classified as follows: (1) Reverse ion exchange water (Ca–Mg–Cl type), (2) Recharging water (Ca–Mg–HCO_3- type), (3) Seawater (NaCl type), (4) Base ion exchange water (Na–HCO_3 type). In alluvial zone, most dominant water type is Ca-Mg-HCO_3, which shifts from 42% to 53% samples from pre to post-monsoon which signifies increase in recharging water (Fig. 11 a & b). Second dominant groundwater type is Na-Cl water type, which shifts from 34% to 24% samples, which signifies decrease in sea water influence from pre to post-monsoon. Na–HCO_3 waters type is less prominent in this zone. In lateritic zone, most dominant water type is Ca-Mg-HCO_3 which shifts from 33% to 27% samples from pre to post-monsoon which signifies decrease in recharging water (Fig. 12a & b). Second dominant groundwater type is Na-Cl water type is increased shifted from 27% to 44% samples ,which signifies increase in sea water influence from pre to post-monsoon.

The dominance of the Na–Cl (Fig. 13a & b) water type is attributed to both seawater intrusion and the recharge of saline water from the nearby rivers (Brindha et al., 2014). The presence of the Na-HCO_3 water type exclusively in the lateritic zone during both pre and post-monsoon periods can be attributed to specific geological or hydrological factors unique to

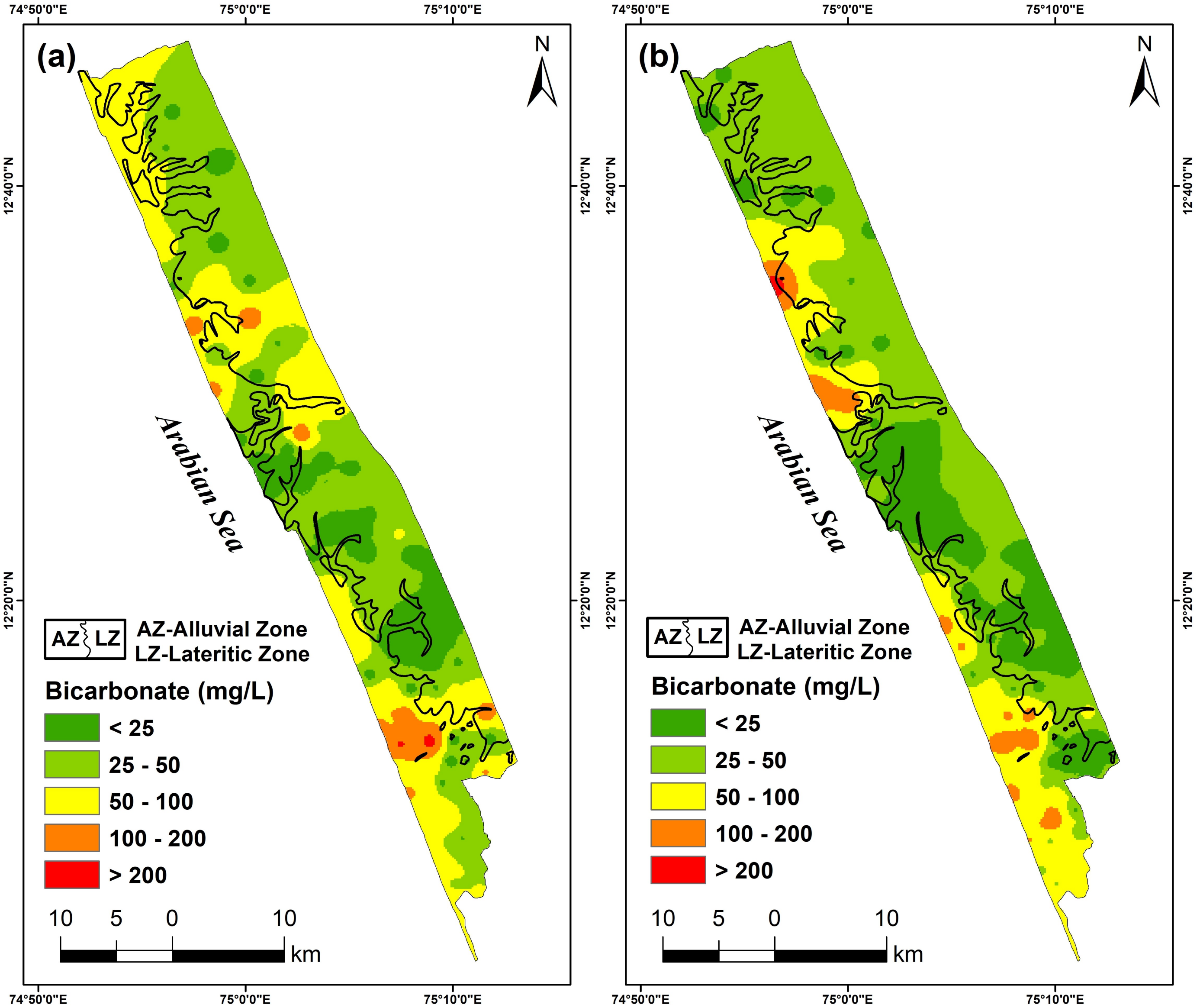

Fig. 7. (a & b) Spatial distribution of bicarbonate in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

that zone. Ca-Mg-HCO_3 is the predominant water type in alluvial zone during pre and post monsoon, especially in the southern coastal belt of the study area.

3.4. Mechanism governing hydrochemistry

Gibbs plot shows the relationship between the precipitations controlled chemical composition of water, rate of evaporation with the lithology of the study area (Gaikwad et al., 2019). Gibbs ratio-I [(Na+ K) / (Na + K+ Ca)] and Gibbs ratio-II [Cl/ (Cl+HCO_3)] are plotted against the Total dissolved solids and are widely used to assess the sources of dissolved chemical constituents such as precipitation dominance, rock dominance and evaporation dominance (Nagaraju et al., 2014). In alluvial zone, Gibbs ratio I values varied from 0.14 to 0.91 during pre-monsoon and values varied from 0.17 to 0.91 during post-monsoon. Gibbs ratio II values varied from 0.08 to 0.99 during pre-monsoon and values varied from 0.16 to 0.94 during post-monsoon.

In lateritic zone, Gibbs ratio I values varied from 0.32 to 0.86 during pre-monsoon and values varied from 0.20 to 0.90 during post-monsoon. Gibbs ratio II values varied from 0.09 to 0.86 during pre-monsoon and values varied from 0.19 to 0.74 during post-monsoon. The samples from this zone were settled in the rock dominance suggesting that the interaction between the groundwater and aquifer material is the major mechanism controlling the water

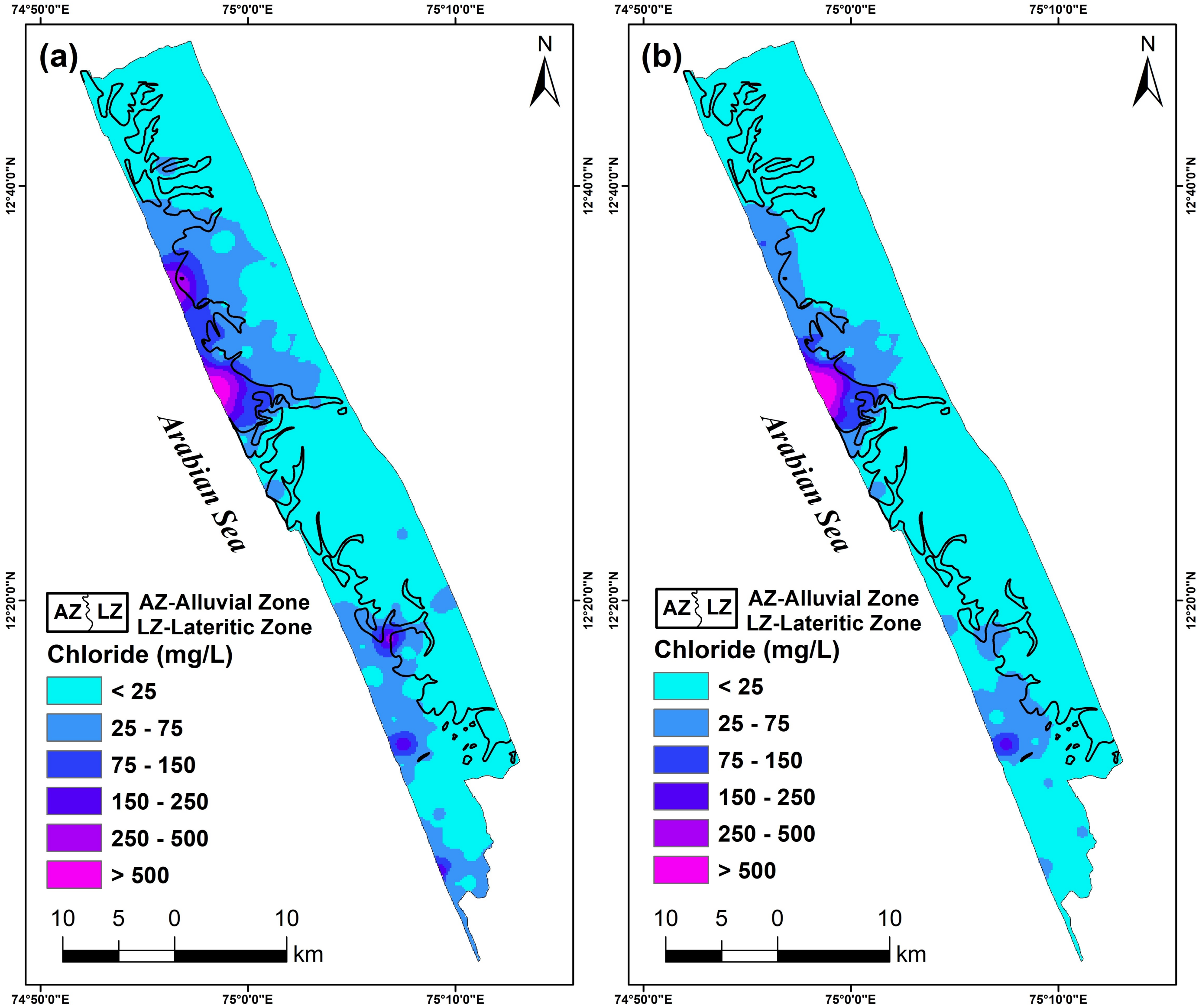

Fig. 8. (a & b) Spatial distribution of chloride in the groundwater during (a) Pre-monsoon (b) Post-monsoon.

chemistry of that zone in both aquifer zones during pre and post-monsoon. The rock-water interaction is influenced by elements such as the local climate and the chemical compositions of the rocks and soils in the area (Girish et al., 2013; Egbueri et al., 2019). In alluvial zone, few groundwater samples from Kasaragod coast are located in evaporation dominant zone during pre and post-monsoon (Fig. 14a & b). Increased evaporation, chemical weathering, and anthropogenic activities elevate Na^+ and Cl^- ions, resulting in high groundwater TDS. This shifts water from rock dominance to the evaporation zone (Fig. 15a & b). The predominant influence of rock weathering on the major ion chemistry of the study area suggests that the weathering of various source rocks produces distinct combinations of dissolved cations and anions in solution (Srinivasamoorthy et al., 2011).

3.5. Ionic ratios

The seasonal variation in ionic concentration of the groundwater geochemistry can be understood when the scatter plot are plotted on X–Y coordinate (Aghazadeh and Mogaddam, 2010; Guler et al., 2002). Many factors influence the quality of water in which the chemical reactions between groundwater and its aquifer lithology have a significant role (Srinivasamoorthy et al., 2014). It provides valuable insights into the hydrogeochemical processes at work in these zones during different seasons, helping to understand the sources and evolution of groundwater

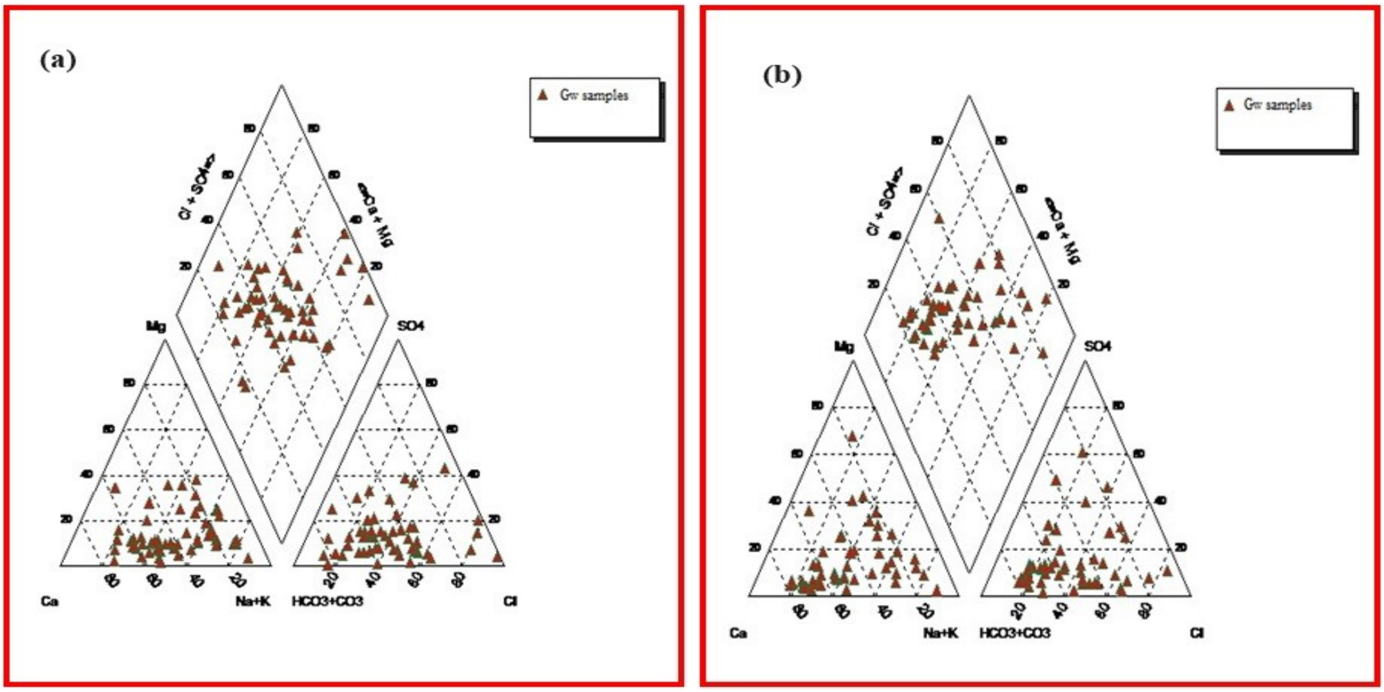

Fig. 9. (a & b) Hill Piper diagram of groundwater in Alluvial zone during (a) Pre-monsoon and (b) Post-monsoon in the study area.

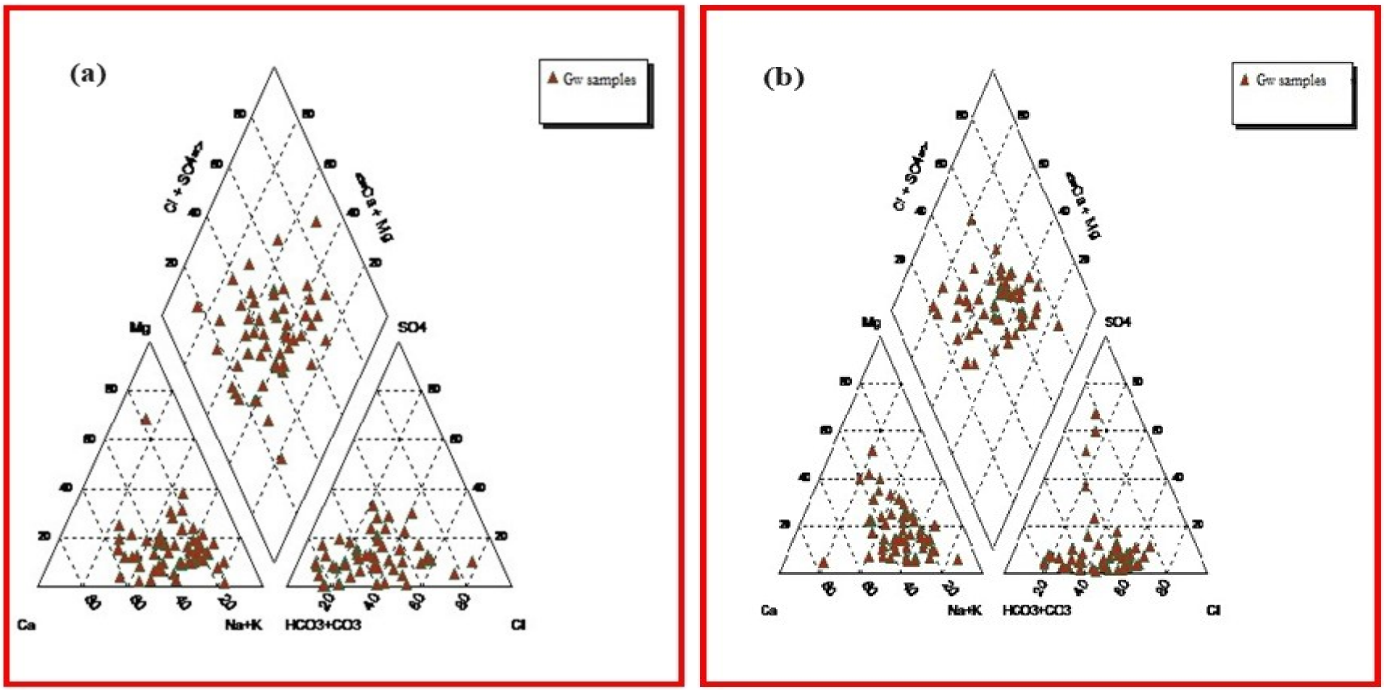

Fig. 10. (a & b) Hill Piper diagram of groundwater in Lateritic zone during (a) Pre-monsoon and (b) Post-monsoon in the study area.

composition (Yang et al., 2020). The scatter plot of Na^+ v/s Cl^- depicts the relationship between these two parameters from alluvial zone and lateritic zone from the study area (Fig. 16 a & b). In Alluvial zone about 73% of pre-monsoon and 44% of post-monsoon, In Laterite zone about 90% of pre-monsoon and 46% of post-monsoon samples have Na/Cl ratio (> 1). Na/Cl molar ratio > 1 signifies Na^+ released from silicate weathering is resulted from rock water interaction (Srinivasamoorthy et al., 2012). Most of the groundwater samples during pre-monsoon fall in or near the equiline and the majority of samples during

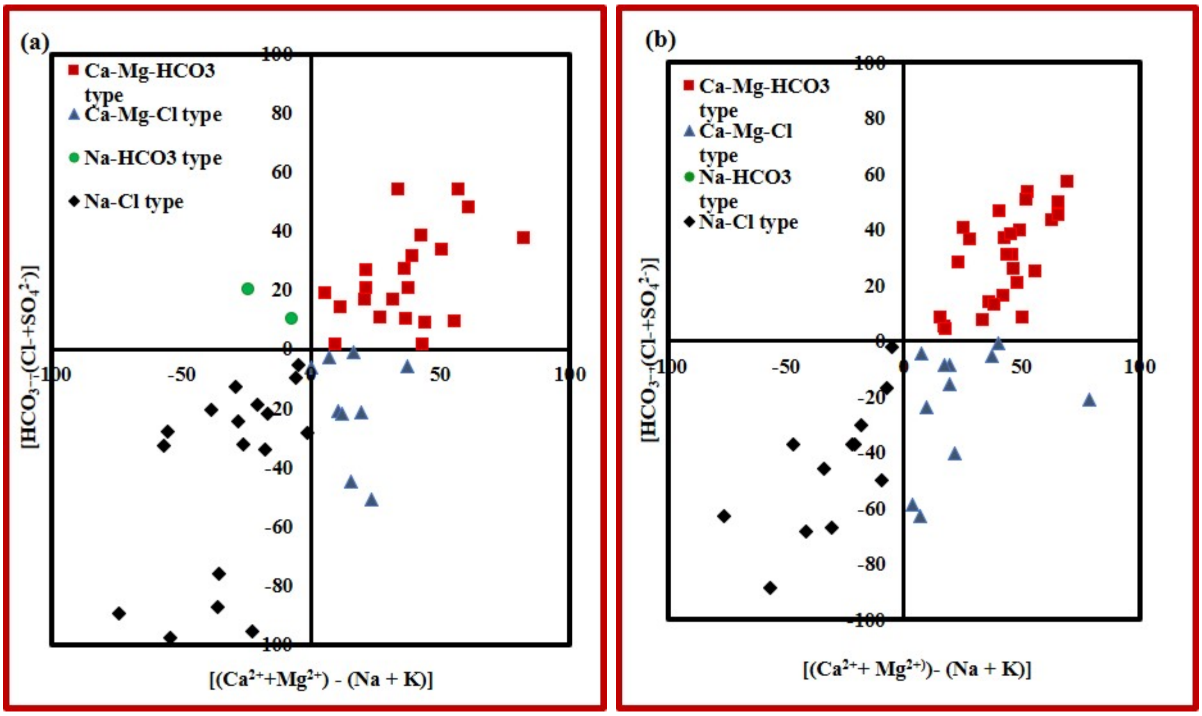

Fig. 11. (a & b) Chadhas plot classification of Alluvial zone during (a) Pre-monsoon and (b) Post-monsoon.

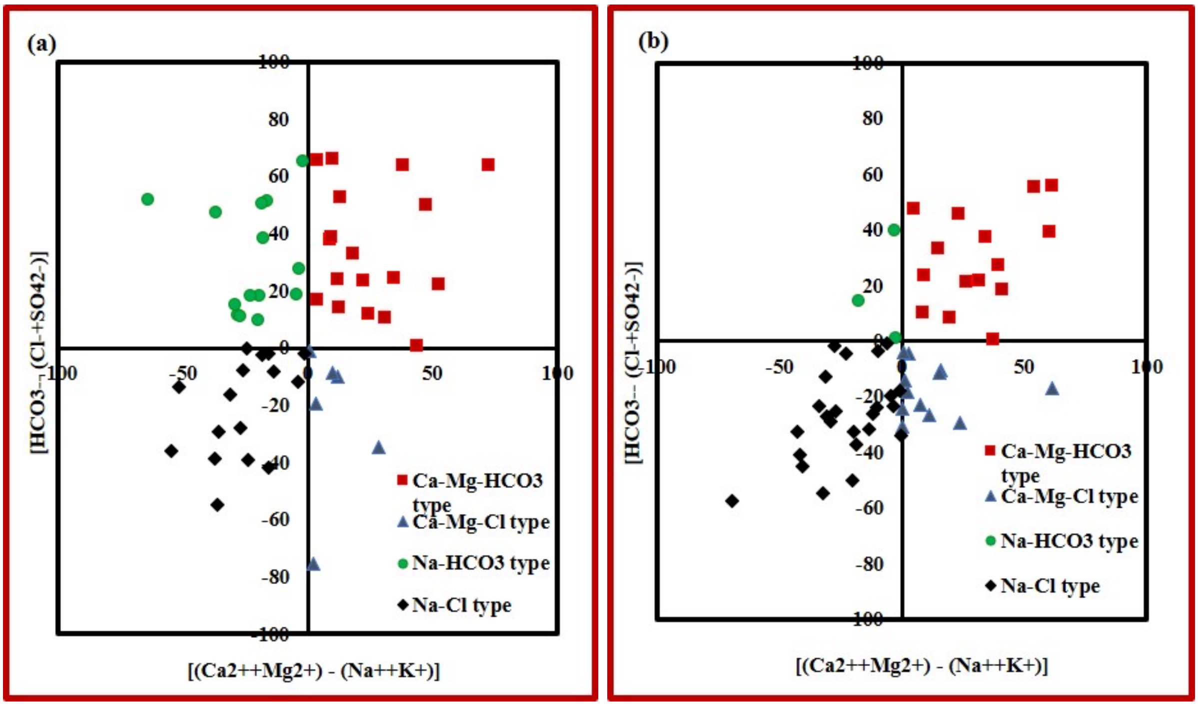

Fig. 12. (a & b) Chadhas plot classification of lateritic zone during (a) Pre-monsoon and (b) Post-monsoon.

post-monsoon fall above the 1:1 equiline. It shows a high correlation for the alluvial zone compared to lateritic zone during pre and post-monsoon indicating combined influence of anthropogenic and lithogenic sources (Gaikwad and Pawar, 2008). Some samples in the alluvial zone exhibit a deviation from the equiline, suggesting that Na^+ originates from distinct sources due to the addition of Cl^- resulting from evaporation. The scatter plot comparing Ca^{2+} + Mg^{2+} versus HCO_3 + SO_4 concentrations in pre-monsoon and post-monsoon groundwater samples from alluvial zone reveals that the majority of samples align closely with the 1:1 line (Fig. 17 a & b). Similar trend is observed in pre-monsoon samples of lateritic zone, but

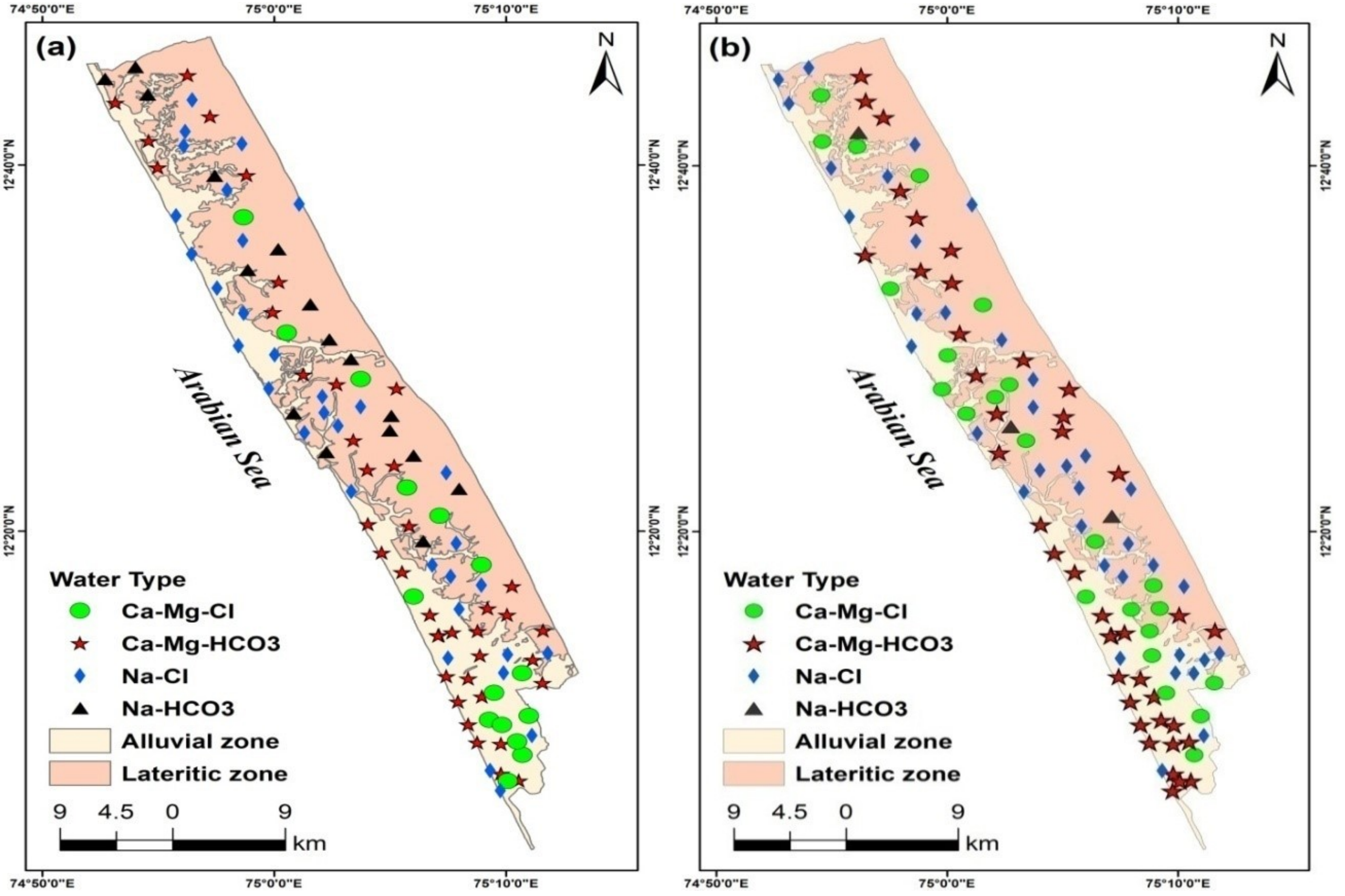

Fig. 13. (a & b) Spatial distribution of the Water type of the groundwater during (a) Pre-monsoon (b) Post-monsoon.

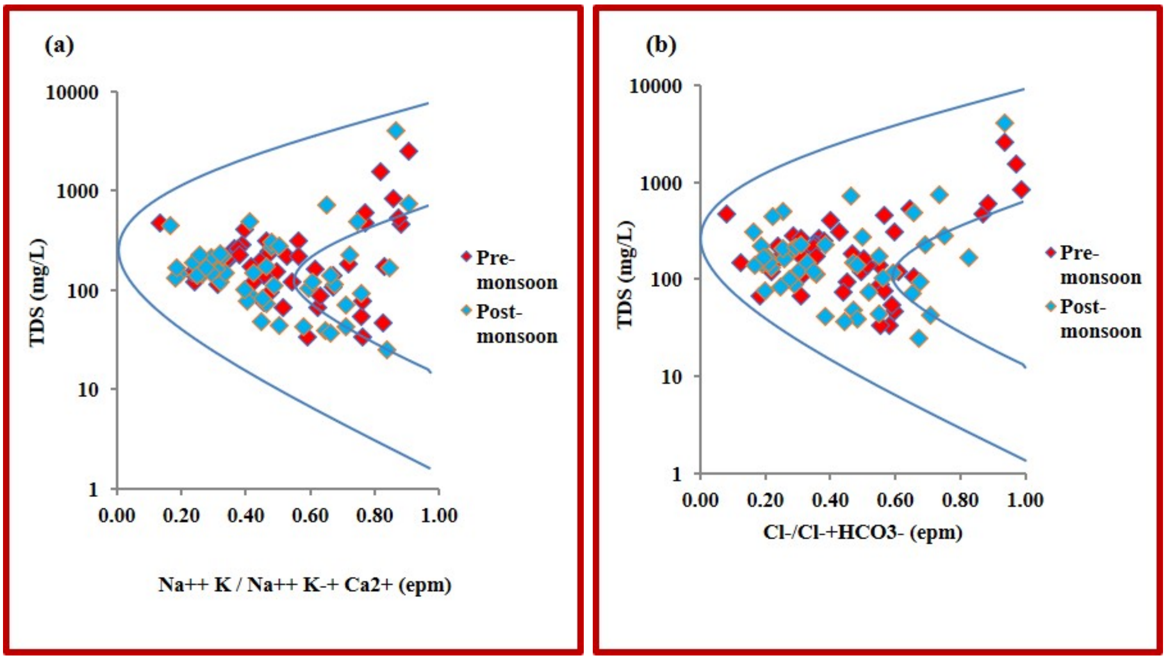

Fig. 14. (a & b) Gibbs diagram of cations and anions in groundwater of Alluvial zone during (a) Pre-monsoon and (b) Post-monsoon in the study area.

majority of samples during post-monsoon fall above the 1:1 equiline, which represents direct ion exchange processes (Aju et al., 2022). The scatter plot diagram of $Na^+ + K^+$ versus Tz^+ is commonly used to con-

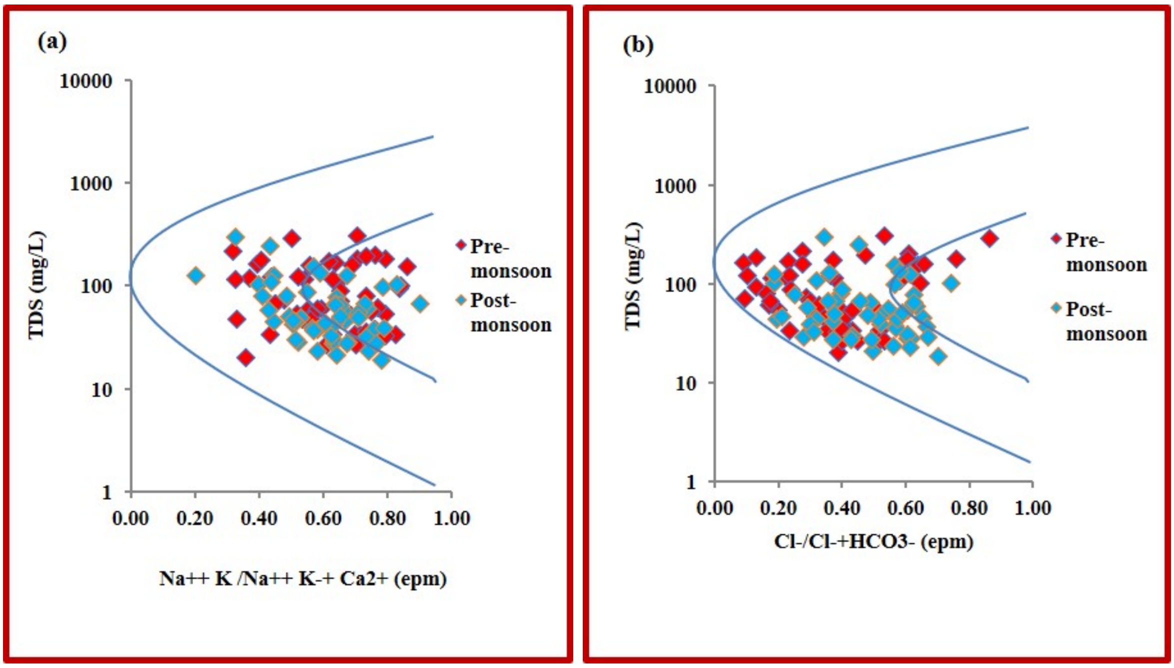

Fig. 15. (a & b) Gibbs diagram of cations and anions in groundwater from Lateritic zone during (a) Pre-monsoon and (b) Post-monsoon in the study area.

firm the presence of sodium and potassium ion in the groundwater along the study area (Fig. 18 a & b). In alluvial zone, the ionic relationship R^2 is greater than 0.9 shows highly positive correlation during pre and post- monsoon. In lateritic zone the ionic relationship R^2 is around 0.5 shows moderate positive correlation during pre and post-monsoon. The excess of Tz^+ ions could be a result of mineral weathering or dissolution (Sarin et al., 1989; Kumar et al., 2018). The scatter plot of SO_4^{2-} versus Cl^- depicts that majority of samples are positioned above the equiline, indicating a dominance of chloride over sulphate (Fig. 19 a & b).

The ion exchange mechanism takes place between the groundwater and the aquifer media during infiltration using Chloro alkaline indices (Schoeller, 1967). CAI I and CAI II were calculated using the following equation. All parameters are in meq/l.

$$\text{CAI I} = (\text{Cl- } (\text{Na+K})) \,/\, \text{Cl}$$
$$\text{CAI-II} = [\text{Cl - } (\text{Na+K})] \,/\, (\text{SO}_4\text{+ HCO}_3)$$

The negative values of CAI-I and CAI-II represent the exchange of $Na^+ + K^+$ from the aquifer media with Ca^{2+} and Mg^{2+} in groundwater (Fisher and Mullican, 1997), which resulting in reverse ion exchange reaction. The positive values represent the exchange of $Na^+ + K^+$ in groundwater exchanges with $Mg^{2+} + Ca^{2+}$ in the aquifer media, which resulting in direct ion exchange (Schoeller, 1967). A negative value also signifies low residence time in the zone (Freeze and Cherry, 1979).In alluvial zone, during pre-monsoon 90% and in post monsoon 66% samples were showing negative CAI-I and CAI-II values, which indicates that dominance of reverse ion exchange process. The remaining 10% and 34% shows positive index values in the groundwater during pre and post-monsoon indicating the occurrence of direct ion exchange (Fig. 20 a & b).

In Lateritic zone, during pre-monsoon, 93% and in post monsoon 82% were showing negative CAI-I and CAI-II values indicating the dominance of reverse ion exchange process in this zone (Fig. 21 a & b). The remaining 7% and 18% shows positive values in the groundwater during pre and post-monsoon indicating the occurrence of direct ion exchange. Reverse ion exchange have a dominant role in the chemical composition of the groundwater in the lateritic zone and alluvial zone. Similar findings were observed in both alluvial and charnockite aquifers at Kozhikode coast (Jesiya and Gopinath, 2019).

3.6. Statistical analysis

The Pearson's correlation matrix is a multivariate statistical method which illustrates the interrelationship between two variables of different chemical parameters. The results of the correlation analysis are considered in the subsequent interpretation. The inverse relationships between chemical parameters are indicated by negative values and $r = 0$ in-

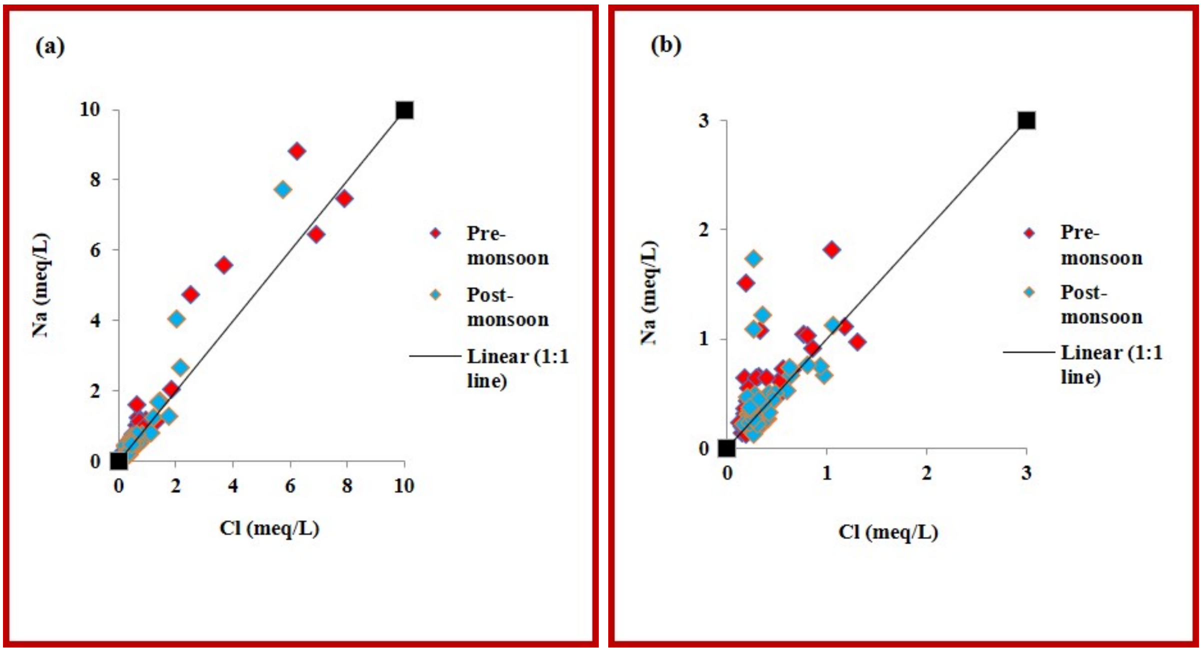

Fig. 16. (a & b) Ions scatter diagram between Na^+ with Cl^- of the (a) Alluvial zone (b) Lateritic zone during Pre and Post-monsoon.

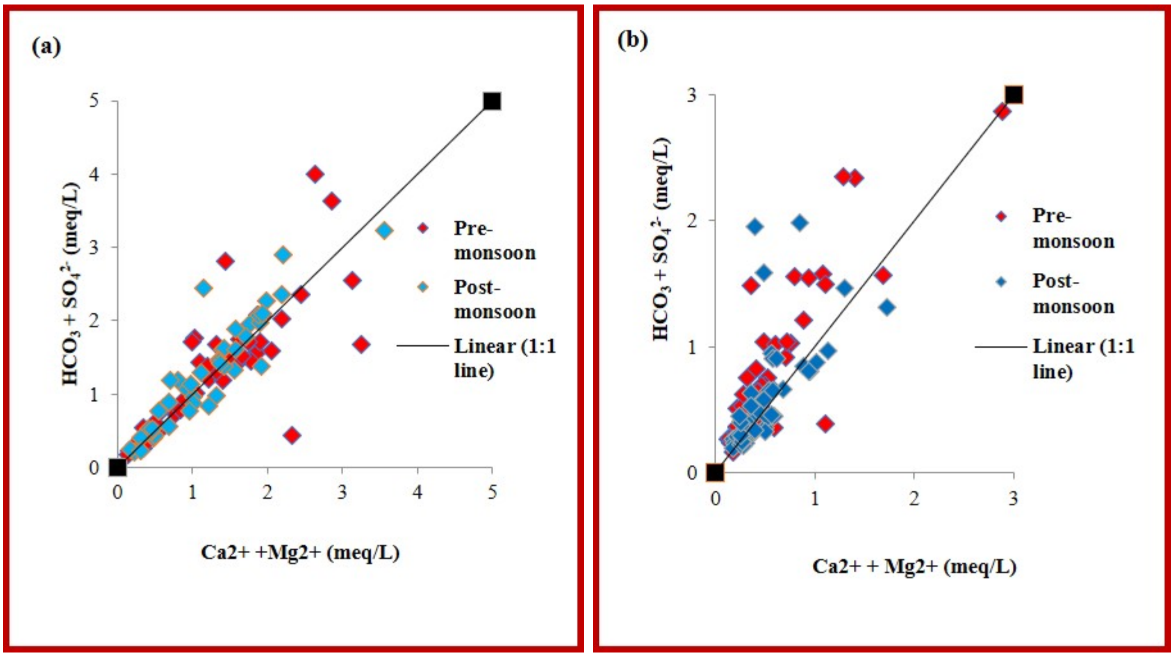

Fig. 17. (a & b) Ions scatter diagram between HCO_{3-}+ SO_4^{2-} with Ca^{2+} + Mg^{2+} in the groundwater of the (a) Alluvial zone (b) Lateritic zone during pre and post-monsoon.

dicates no relationship between the parameters. In alluvial zone, EC has a strong positive correlation with Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- during pre-monsoon which indicates the impact of multiple processes such as ion exchange, mineral dissolution and anthropogenic activities like use of fertilizers and sewage disposal over the water chemistry (Khan et al., 2020). A strong positive correlation with Ca^{2+}, Cl^-, and HCO_{3-} during the post-monsoon indicates the mobility of ions. This indicates the significant influence of these ions on groundwater chemistry throughout both seasons. The EC plays a crucial role in governing the groundwater quality in the study area. The extremely strong positive correlation between EC and TDS in the pre and post-monsoon season indicates that the groundwater primarily con-

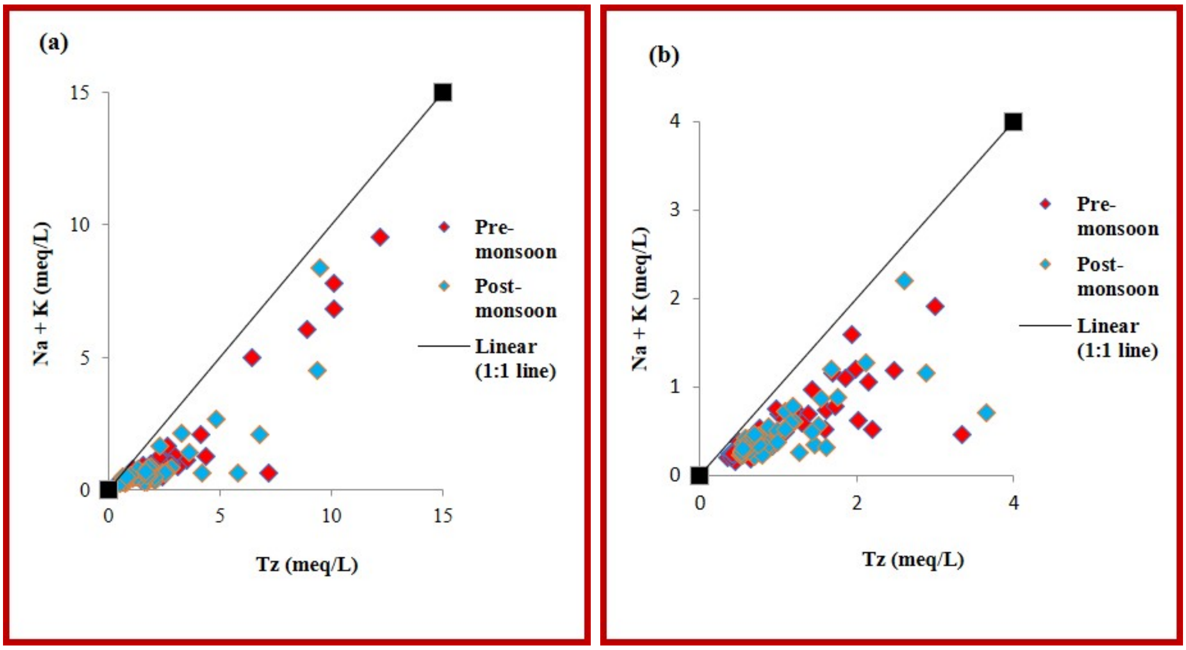

Fig. 18. (a & b) Ions scatter diagram between Na + K with Tz of the (a) Alluvial zone (b) Lateritic zone during Pre and Post-monsoon.

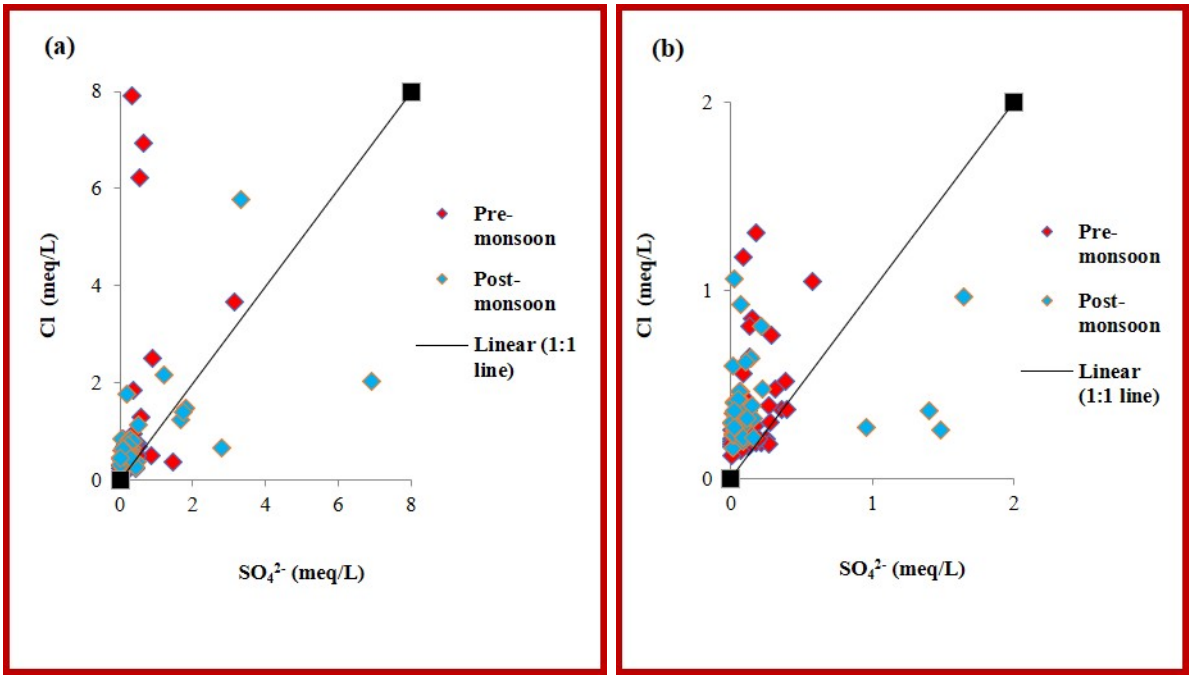

Fig. 19. (a & b) Ions scatter diagram between SO_4 with Cl^- of the (a) Alluvial zone (b) Lateritic zone during Pre and Post-monsoon.

sists of charged soluble components (Khan et al., 2020). Positive correlation between the ions indicates that the ions are from the same source. Cl^- has strong positive correlation with SO_4^{2-} during pre-monsoon and good positive correlation during post-monsoon (Table 2, 3). Na^+& K^+ was in strong positive correlation with Cl^- during pre-monsoon. During post-monsoon, Cl^- has perfect correlation with Na^+ indicates the possibilities of saline water intrusion (Srinivasamoorthy et al., 2011). Na^+ and K^+ show a poor positive correlation with HCO_{3-} during both seasons. Mg^{2+} show good positive correlation during pre-monsoon and strong positive correlation with Ca^{2+} during post-monsoon. The positive relationship indicates mineral dissolution and cation exchange during seawater ingress (Khan et al., 2021).

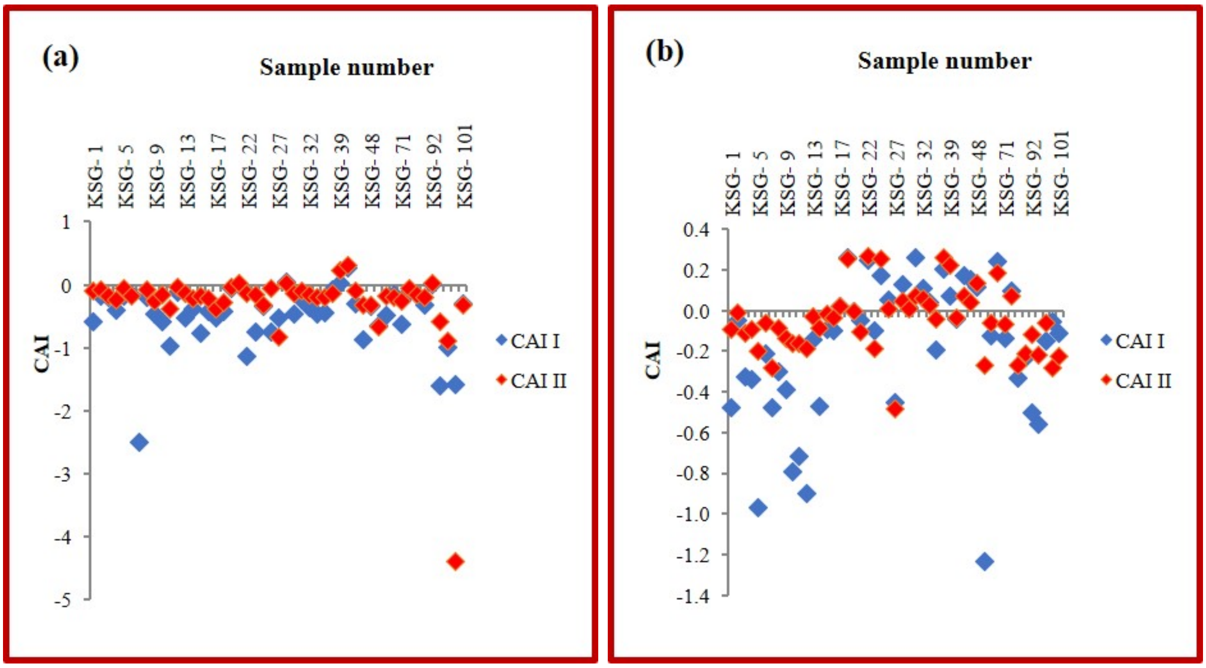

Fig. 20. (a & b) CAI I and CAI II of groundwater samples in Alluvial zone during (a) Pre-monsoon and (b) Post-monsoon.

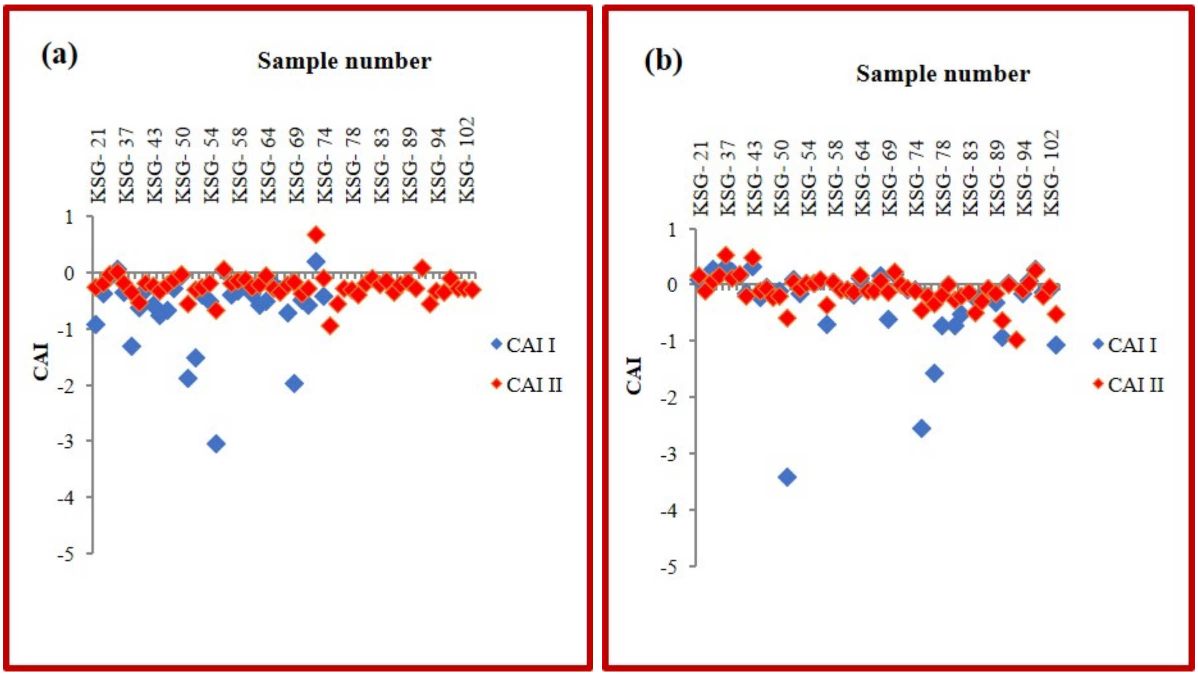

Fig. 21. (a & b) CAI I and CAI II of groundwater samples in Lateritic zone during (a) Pre-monsoon and (b) Post-monsoon.

In lateritic zone, EC has a strong positive correlation with Na^+, Cl^- and Ca^{2+} during pre-monsoon and strong positive correlation with Ca^{2+}, Cl^- and HCO_3- during the post-monsoon is due to the dissolution of salts contribute to an increase in electrical conductivity (Wagh et al., 2016). Na^+ and K^+ with Ca^{2+} and Mg^{2+} are in poor positive correlation during pre and post-monsoon. $SO_4{}^{2-}$ has poor positive correlation with HCO_3- and Cl^- is in a poor positive correlation during both pre and post monsoon. Cl^- with Na^+ was in good positive correlation and poor positive correlation with K^+ during pre-monsoon and was in poor positive correlation with both ions during post-monsoon. Na^+& K^+ were showing poor positive correlation during both seasons with HCO_3-. Non-competitive ions like Na^+& K^+ were showing poor positive correlation during pre-monsoon and strong positive correlation during post-monsoon

Table 2. Correlation matrix for the hydrochemical parameters of the Alluvial zone groundwater samples during Pre-monsoon.

Pre Monsoon	**pH**	**EC**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
pH	1.00									
EC	0.34	1.00								
TDS	0.34	**1.00**	1.00							
Na^+	0.32	**0.95**	**0.95**	1.00						
K^+	0.31	**0.85**	**0.85**	**0.92**	1.00					
Ca^{2+}	0.49	**0.73**	**0.73**	0.60	0.56	1.00				
Mg^{2+}	0.21	**0.71**	**0.71**	0.51	0.41	0.64	1.00			
HCO_{3-}	0.41	0.24	0.24	0.19	0.28	0.64	0.28	1.00		
SO_4^{2-}	0.40	**0.91**	**0.91**	**0.87**	**0.79**	**0.71**	0.68	0.20	1.00	
Cl^-	0.28	**0.97**	**0.97**	**0.99**	**0.89**	0.61	0.59	0.15	**0.86**	1.00

Table 3. Correlation matrix for the hydrochemical parameters of the Alluvial zone groundwater samples during Post-monsoon.

Post Monsoon	**pH**	**EC**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO^{3-}**	**SO_4^{2-}**	**Cl^-**
pH	1.00									
EC	0.22	1.00								
TDS	0.21	**1.00**	1.00							
Na^+	0.18	**0.99**	**0.99**	1.00						
K^+	0.05	0.08	0.08	0.03	1.00					
Ca^{2+}	0.41	**0.85**	**0.85**	**0.77**	0.12	1.00				
Mg^{2+}	0.15	**0.84**	**0.84**	**0.78**	0.13	**0.77**	1.00			
HCO_3^-	0.46	0.47	0.47	0.36	0.40	**0.73**	0.63	1.00		
SO_4^{2-}	0.13	**0.70**	**0.71**	0.64	0.52	0.68	**0.74**	0.52	1.00	
Cl^-	0.17	**0.98**	**0.98**	**1.00**	0.00	**0.77**	**0.77**	0.34	0.60	1.00

Table 4. Correlation matrix for the hydrochemical parameters of the Lateritic zone samples during Pre-monsoon.

Pre Monsoon	**pH**	**EC**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
pH	1.00									
EC	0.28	1.00								
TDS	0.28	**1.00**	1.00							
Na^+	0.12	**0.74**	**0.74**	1.00						
K^+	0.46	0.48	0.48	0.43	1.00					
Ca^{2+}	0.32	**0.72**	**0.72**	0.41	0.52	1.00				
Mg^{2+}	0.30	0.28	0.28	0.11	0.35	0.30	1.00			
HCO^{3-}	0.35	0.41	0.41	0.40	0.54	0.58	**0.74**	1.00		
SO_4^{2-}	0.12	0.55	0.55	0.52	0.57	0.69	0.25	0.40	1.00	
Cl^-	0.11	**0.82**	**0.82**	0.69	0.30	0.45	0.06	0.05	0.39	1.00

Table 5. Correlation matrix for the hydrochemical parameters of the Lateritic zone groundwater samples during Post-monsoon.

Post Monsoon	**pH**	**EC**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO^{3-}**	**SO_4^{2-}**	**Cl^-**
pH	1.00									
EC	0.22	1.00								
TDS	0.22	**1.00**	1.00							
Na^+	0.00	0.43	0.43	1.00						
K^+	-0.05	0.08	0.08	**0.72**	1.00					
Ca^{2+}	0.37	**0.86**	**0.86**	0.38	0.01	1.00				
Mg^{2+}	0.05	0.69	0.68	0.10	-0.01	0.53	1.00			
HCO_3^-	0.45	**0.79**	**0.79**	0.29	0.04	**0.91**	0.68	1.00		
SO_4^{2-}	-0.12	0.38	0.38	**0.73**	0.55	0.40	0.48	0.43	1.00	
Cl^-	0.12	**0.80**	**0.80**	0.43	0.05	0.58	0.39	0.42	0.21	1.00

(Table 4, 5).

3.7. Factor analysis

Factor analysis is a most commonly used multivariate statistical method in groundwater studies (Chaudhry et al., 2019). A higher factor loading indicates a more substantial contribution of the variable to that specific factor. Varimax orthogonal rotation with Kaiser normalization for factor loadings, a high loading was defined as greater than 0.75, and a moderate loading was defined as 0.40 - 0.75 loadings of less than 0.40 were considered insignificant

Table 6. Factor analysis of the Alluvial zone during Pre and Post-monsoon.

Alluvial zone	**Pre-monsoon**		**Post-monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
pH	0.189	**0.701**	0.137	0.475
EC (µS/cm)	**0.962**	0.242	**0.979**	0.179
TDS (mg/l)	**0.962**	0.242	**0.979**	0.178
Na^+ (ppm)	**0.960**	0.138	**0.978**	0.073
K^+ (ppm)	**0.871**	0.183	-0.105	**0.787**
Ca^{2+} (mg/l)	0.562	**0.729**	**0.799**	0.449
Mg^{2+} (mg/l)	0.622	0.355	**0.822**	0.348
HCO_3- (mg/l)	0.027	**0.889**	0.357	**0.800**
SO_4^{2-} (ppm)	**0.898**	0.266	0.620	0.578
Cl- (mg/l)	**0.978**	0.109	**0.981**	0.037
Variability (%)	60.333	21.924	56.925	22.112
Cumulative (%)	60.333	82.257	56.925	79.037

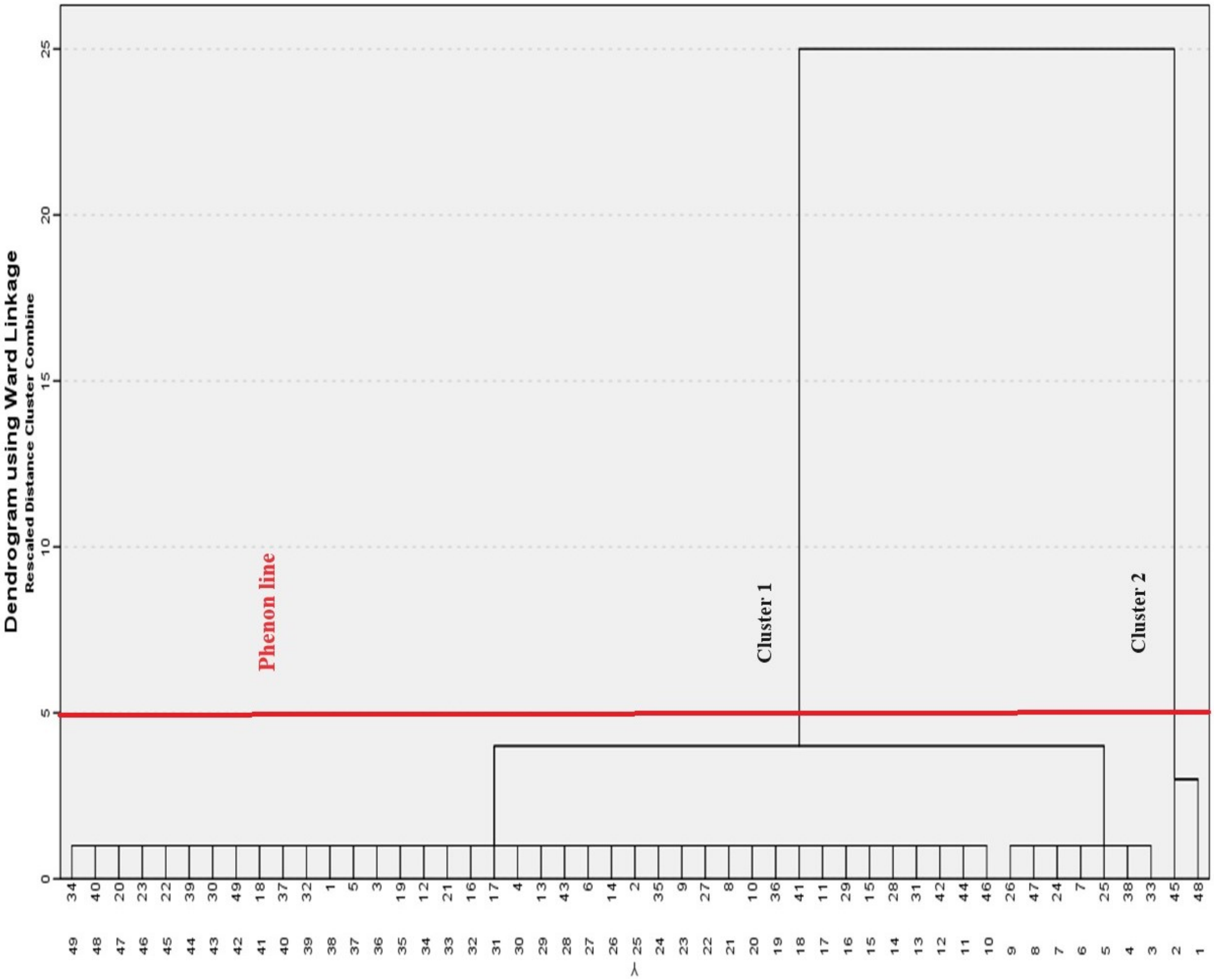

Fig. 22. Dendrogram shows sampling site clusters in Alluvial zone during Pre-monsoon.

(Amadi et al., 2012).In the Alluvial zone, Factor-1 is accounted for 60.3% of the variance, exhibits strong positive loadings for EC, TDS, Na, K, Cl⁻, and SO_4^{2-} (Table 6). It is suggesting that these interactions may be the most significant mechanisms determining the groundwater quality of the area. Factor-1 exhibits the highest loading for Na^+ and Cl^- ions, indicating a significant contribution from the dissolution of chlorides and sulfates processes.

Factor-2 explained 21.9% of the variance with the

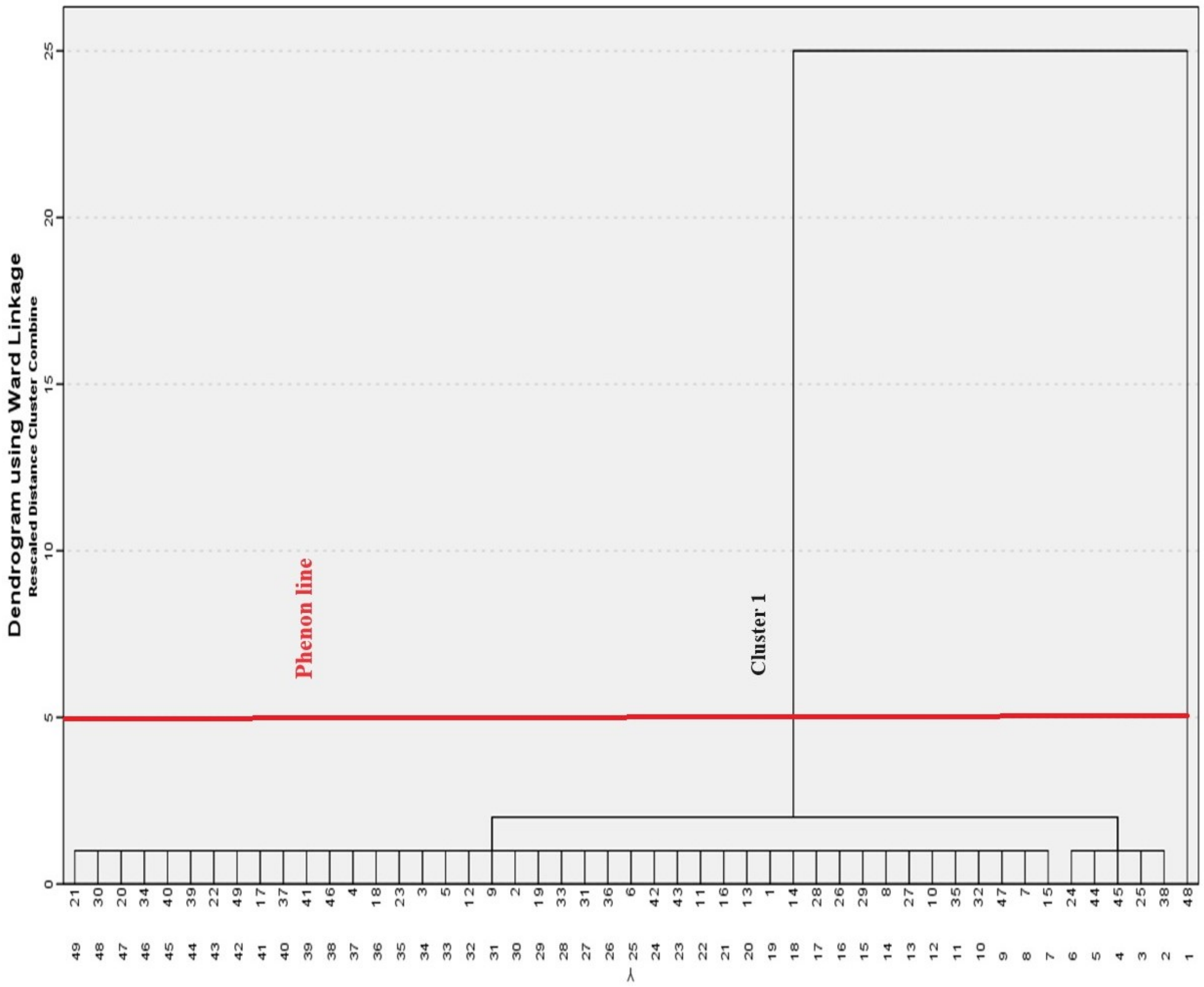

Fig. 23. Dendrogram shows sampling site clusters in Alluvial zone during Post-monsoon.

variables pH, Ca^{2+} and HCO_3-. The significant loading of pH indicates that the concentration of HCO_{3}- ions plays a crucial role in controlling pH of the water (Srivastava and Ramanathan, 2008). During post-monsoon, Factor-1 has 56.9% of the variance with the variables, EC, TDS, Na^+, Cl^-, Ca^{2+} and Mg^{2+}.The major ions most closely associated with TDS, particularly in relation to their correlation, include calcium, chloride, sodium, and magnesium (Thirumalini and Joseph, 2009). The origin of TDS components and the EC of water depend on diverse geological processes, including dilution and leaching (Rusydi, 2019).Factor-1 exhibits the highest loading for Na^+ and Cl^- ions, indicating dissolution of chlorides and sulfates processes. The minerals in the soil will be leached by sewage water that seeps through the soil column (Ravikumar and Somashekar, 2012). During post-monsoon, variance is 21.1% and strong contributing variables are K^+ and HCO_3-. Potassium primarily originates from minerals such as orthoclase, commonly found in fertilizers applied in agricultural practices, and the decomposition of organic wastes (Saha et al., 2019).

In lateritic zone, during pre-monsoon, Factor-1 accounts for 41.8% of variance and strong positive loading variables are EC, TDS, Na^+ and Cl^-. During post-monsoon, factor-1 has 48.2% of the variance and strong contributions by the variables, EC, TDS, Ca^{2+}, Mg^{2+}, and HCO_3- (Table 7). EC and TDS in the study area are mainly controlled by Ca^{2+}, Mg^{2+}, and HCO_3-ions present in the water. Ion exchange and solution activity play a crucial role in determin-

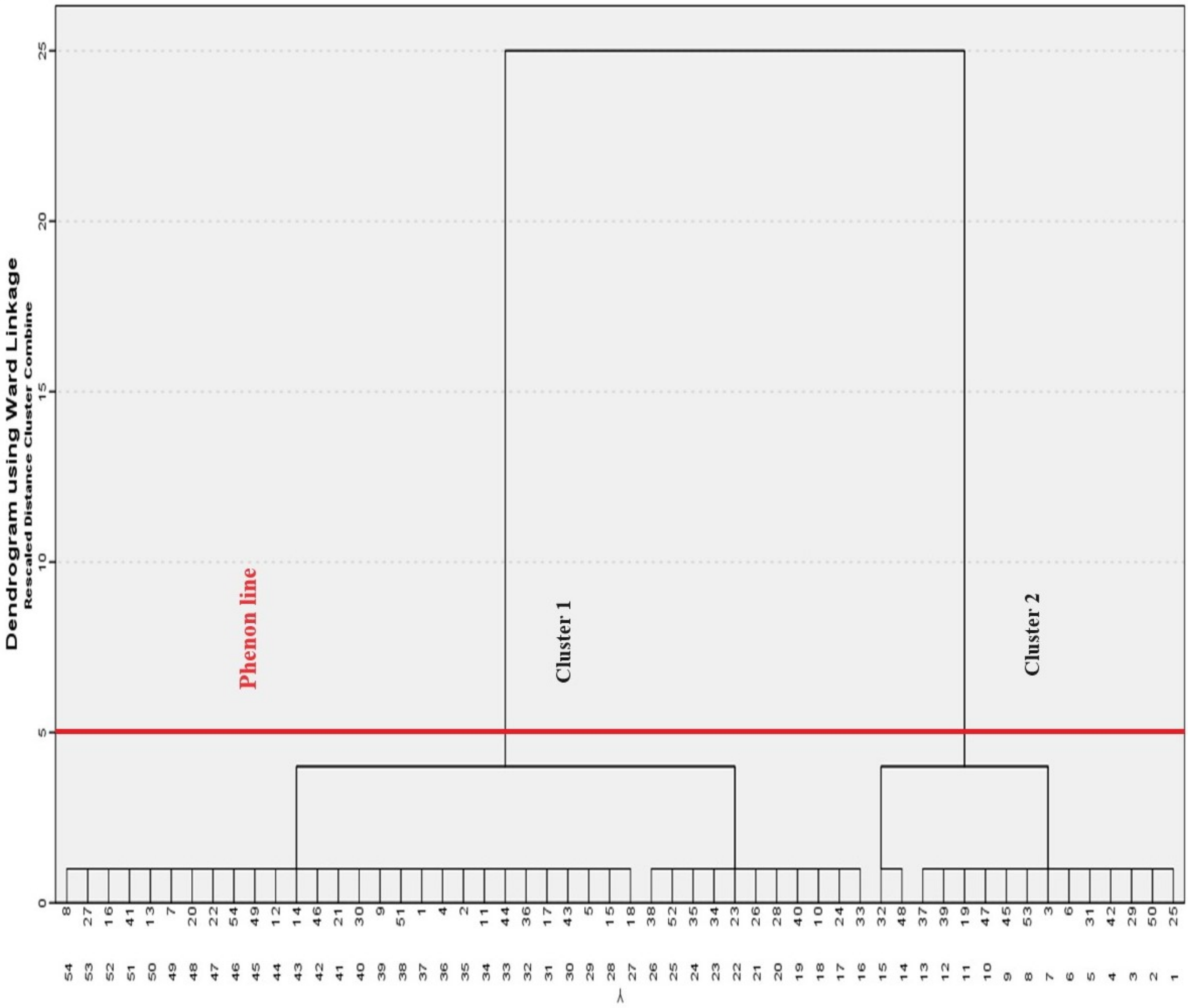

Fig. 24. Dendrogram shows sampling site clusters in Lateritic zone during Pre-monsoon.

ing the concentration of EC in groundwater (Zacheus and Martikainen, 1997). High loadings on Ca^{2+} suggest silicate weathering, while the presence of HCO_3^- can be attributed to the reaction of silicate minerals with CO_2 in rainwater and soil (Paulami et al., 2016). High loadings of Cl^- than Na^+ suggest the influence of marine sources or anthropogenic activities such as wastewater discharge (Ferchichi et al., 2018). Factor-2 explained 27.9% of the variance and strong contributions are from Mg and HCO_3-. In addition, this component had positive moderate contributions by the variables pH, K^+, Ca^{2+} and SO_4^{2-} during pre-monsoon. During post-monsoon, Factor-2 accounts for 24.13% and strong contributing variables are Na^+, K^+ and SO_4^{2-}. In post-monsoon the processes of dissolution and mixing factors, plays a significant role in variations in the factors and alterations in the loadings of each variable.

3.8. Hierarchical Cluster analysis

Hierarchical Cluster analyses (HCA) is to identify similarities and differences in measured analytical data using the Ward's linkage method. R-mode HCA was conducted to categorize parameters into groups based on their similarity (Gampson et al., 2017). In alluvial zone, during pre-monsoon Cluster-1 is having 47 samples which is observed as having negligible pollution and low contamination levels and Cluster-2 having couple of samples having high pollution and contamination levels. Cluster-1 is differentiated from Cluster-2 due to its large linkage distance during the pre-monsoon (Fig. 22). The Cluster-1 comprises 96%

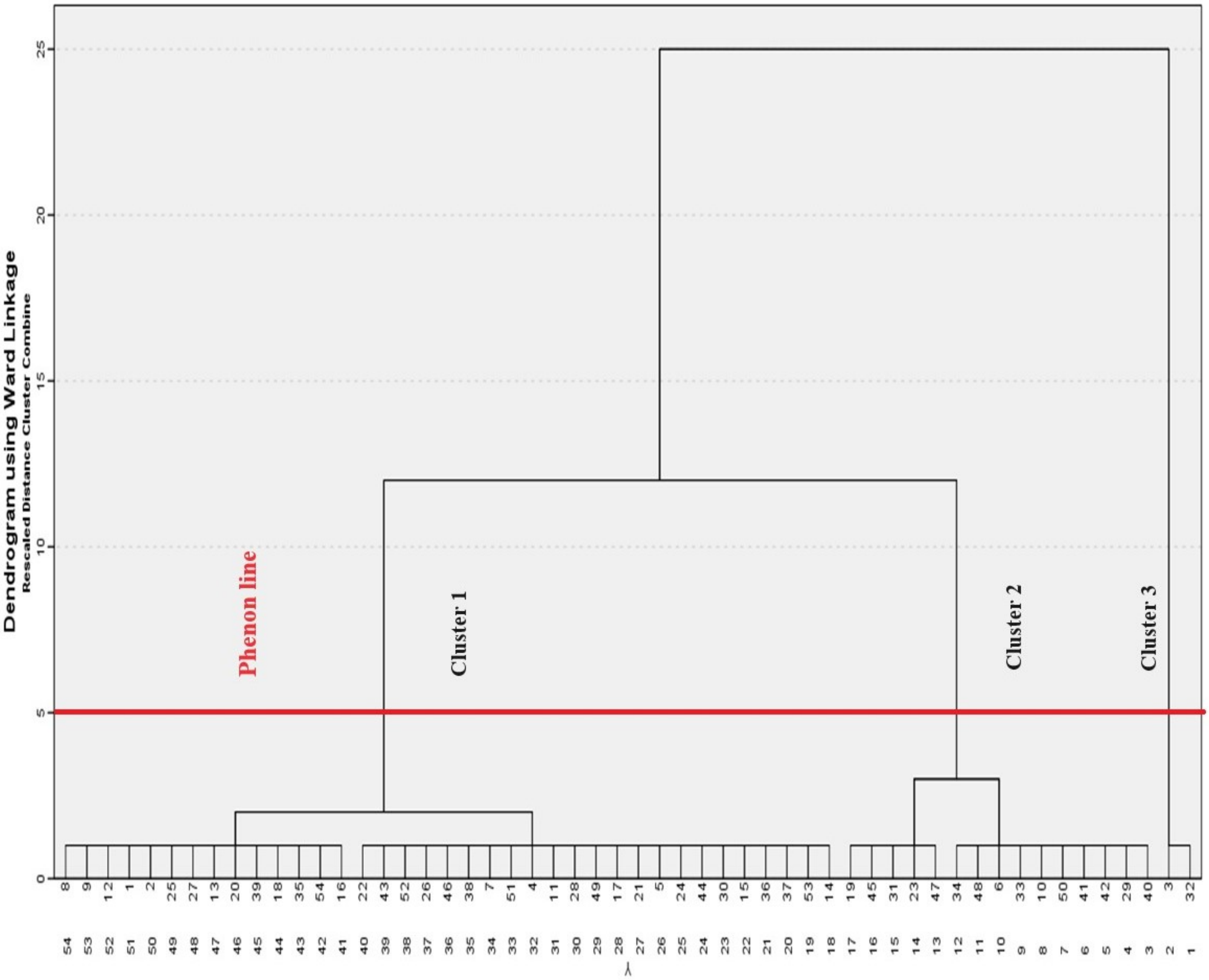

Fig. 25. Dendrogram shows sampling site clusters in Lateritic zone during Post-monsoon.

Table 7. Factor analysis of the Lateritic zone during Pre-monsoon and Post-monsoon.

Lateritic zone	**Pre-monsoon**		**Post-monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
pH	0.101	0.587	0.399	-0.260
EC (µS/cm)	**0.923**	0.267	**0.950**	0.193
TDS (mg/l)	**0.923**	0.267	**0.950**	0.192
Na^+ (ppm)	**0.823**	0.130	0.265	**0.887**
K^+ (ppm)	0.413	0.643	-0.093	**0.874**
Ca^{2+} (mg/l)	0.630	0.527	**0.916**	0.121
Mg^{2+} (mg/l)	0.009	**0.812**	**0.724**	0.100
HCO_3- (mg/l)	0.190	**0.881**	**0.894**	0.095
SO_4^{2-} (ppm)	0.603	0.402	0.314	**0.809**
Cl- (mg/l)	**0.910**	-0.094	**0.718**	0.180
Variability (%)	41.884	27.996	48.21	24.13
Cumulative (%)	41.884	69.881	48.21	72.34

of water suitable for drinking, whereas the Cluster-2 includes 4% of water categorized as unsuitable for human consumption. During post-monsoon, cluster-1 comprises 96% of water suitable for drinking, whereas the Cluster-2 includes 4% of water categorized as unsuitable for human consumption (Fig. 23).

In lateritic zone, during pre-monsoon Cluster-1 is having 39 samples and Cluster-2 is having 15 samples. The cluster-1 comprises 72% and cluster-2 includes 28% of water categorized as suitable for human consumption. Cluster-1 is differentiated from Cluster-2 due to its large linkage distance (Fig. 24). During post-monsoon, the cluster-1 comprises 68% and cluster-2 as 28% samples suitable for human consumption and 4% of samples are categorized as unsuitable for human consumption due to anthropogenic activity. Clusters-1 and Cluster-2 is having short linkage distance, suggesting similar hydrogeochemical components in groundwater. The Cluster-3 is geochemically more distinct than cluster-1 and cluster-2 since it has high linkage distance during post-monsoon (Fig. 25). A similarity is evident among most of the samples in both aquifer systems.

4. CONCLUSION

The present study examined the spatio-temporal variation and to understand the hydrogeochemical aspects of groundwater of alluvium and lateritic zones of study area in coastal and inland zones of Kasaragod district. A significant variation in hydrogeochemistry is observed during pre and post-monsoon season. Hill-Piper diagrams show that Ca-Mg-HCO_3 is dominant water types irrespective of seasons in alluvial zone. In lateritic zone, Ca-Mg-HCO_3 water type dominates during pre-monsoon and Na-K-Cl-SO_4 during post-monsoon and it indicates that dissolution of mixing zone during both the pre and post-monsoon. The observation of Chadha plot also aligns with the conclusions drawn from Hill-piper plot. The Gibbs plot highlights that the majority of samples are influenced by rock-water interaction dominance and precipitation, with only a few exhibiting evaporation dominance. Chemical weathering and mineral dissolution are the major factor that controls the groundwater chemistry of the study area. This trend is consistent in both alluvial and lateritic zones. The Na-Cl water type signifies a reduction in seawater influence from the pre-monsoon to the post-monsoon period, particularly in the alluvial zone. In CAI majority of samples show reverse ion exchange in both seasons at both zones. The Pearson's correlation matrix shows a strong positive correlation of EC with most of the ions in both alluvial zone and lateritic zone during pre-monsoon compared with post monsoon. In factor analysis total variance had strong positive loading on EC, TDS, Na^+ and Cl^- during pre-monsoon and Ca^{2+}, Mg^{2+}, HCO_{3-} during post-monsoon. About 2 major Clusters were found in both alluvial and lateritic zones. The similar hydrochemical characteristics were observed from the cluster analysis of the study area. Majority of the groundwater samples falls in the suitable for drinking category and a very few samples are exceeding the limits due to some anthropogenic activities. The order of cation dominance is Na $>$ Ca $>$ Mg $>$ K and, anion dominance is $HCO_3 > Cl > SO_4$ during pre and post-monsoon in both alluvial zone and lateritic zone.

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