International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 11 ǁ November 2022 ǁ PP. 28-44

Hydrogeochemical and Microbiological Condition in Mangrove Environment of Tuticorin Coast, Tamilnadu, India

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Abstract

Mangrove water and sediments, and groundwater samples were collected from different locations in three Sites including Kallar estuary, Tuticorin creek and Pazhayakayal estuary. The present study pertains to the physico-chemical characteristics of the mangrove sediments, water and groundwater of coastal zone between Tuticorin and Pazhayakayal. Sampling points were limited to ten for surface water, sediment collection and groundwater collection. The periodicity of sampling was seasonal i.e. pre-monsoon (April 2005 to June 2005) and post monsoon (February 2006 to April, 2006). The collected mangrove water and groundwater samples were filtered and acidified with nitric acid for analysis. The samples were analysed for concentrations of major components namely calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K), carbonate (CO_3), bicarbonate (HCO_3), chloride (Cl) and sulphate (SO_4) and minor elements.

The above study reveals that hydrochemical processes, river water input, irrigation return flow and influence of contaminated marine water might have contributed more ions to groundwater. However, the groundwater is not much affected in this study area. An at least now serious step has to be taken to protect the mangrove environment along the Tuticorin coast. This may improve the mangrove environment, marine organisums, as well as the coastal aquifer system.

Keywords: *Groundwater, Mangrove, Geochemistry and Environment etc.*

Date of Submission: 25-10-2022 Date of acceptance: 05-11-2022

I. Introduction

Estuaries, bays and lagoons are transitional littoral zone between the sea and the land, having developed by the changes in sea level during the Holocene period. Coastal zones cover only 8% of the ocean surface and less than 5% of the ocean volume but are responsible for 18 to 33% of the total ocean production. They also play an important role in ecology of the sea. Those environmental characteristics have turned most coastal environments into ideal for fisheries, aqua culture and tourism, eventually followed by accelerated urbanization. Hence, anthropogenic fluxes of materials are higher than the natural flux in many coastal areas that poses severe threat to coastal ecosystem, inhabited significantly by mangroves and further, it affects the groundwater quality of the coastal zone. Coastal environments are subjected to natural, biological and anthropogenic pressure, causing serious concern on global scale. Mangroves of coastal compartment losing their health as flora and fauna associated stand threatened. The intensity is much larger in estuarine systems associated with mangrove vegetation.

Tuticorin coast is situated along the Gulf of manner Bio-reserve. This coast is known for pearl fishing. Now it is flourished with thermal and various chemical industries. Fluvial and gaseous outputs from these industries are pouring heavy metals and other contaminants into the sea. Pazhayakayal, influenced by the Thamirabarni estuary, south of Tuticorin harbour forms a dumping ground for point and non-point source of Contaminants. Mangrove ecosystem of this estuary is being extremely rugged and damaged. According to murugesan and Sukumaran (2002) “Madura Fabrics” located at Vikramasingapuram discharged more than 10,000 kilo liters of effluents per day into the river Thamiraparani, containing several heavy metals as Mn,Cu,Cr and Fe. The Chloralkali Chemical industry situated near the river mouth pours the potentially toxic mercury into the estuary. The effluents in the form of oil waste are let into the river by the state owned transport corporation to the extent of around 500 litres per day (Martin, 1994). Tuticorin Alkali Chemical (TAC) discharges about 75,000 litres of treated effluent into the sea per day. SPIC lets out about 4, 320 kilo-litres of waste water per day. About 5000 tonnes of fly ash per year from the TTPP is dumped into the sea that disperses along the sea bottom.

All these contaminants are transported by river to the coastal estuary in the form of fluvial inputs. Decreasing river typography gradients at estuary trapped and deposited the contaminants and only a minor fraction of the continental load is exported to the open sea. It is estimated that 75% to 90% of the total flux of continental material to the ocean is trapped in Coastal environment (Berner, 1982). In the view of fast deterioration of mangrove ecosystem and groundwater quality in the coastal environment a careful pollution monitoring is required to stabilize shape lines before human beings were affected. Hence a study requires systematic understanding of biogeochemistry of mangrove ecosystem and groundwater of the coastal environment. A plenty of scientific data are added about coastal environment protection world over, but until now no research data have been reported on the biogeochemistry of the coastal zone between Tuticorin and Pazhayakayal. So, the present study has aimed mainly to understand the physico-chemical characteristics of mangrove sediments, water and groundwater. This work could fill the long felt gap regarding the status of mangrove ecosystem and groundwater environment along the coastal zone of the study area. The present study pertains to the physico-chemical characteristics of the mangrove sediments, water and groundwater of coastal zone between Tuticorin and Pazhayakayal.

II. Study area

Tuticorin coast is situated along the Gulf of manner Bio-reserve. This coast is known for pearl fishing. Now it is flourished with thermal and various chemical industries. Fluvial and gaseous outputs from these industries are pouring heavy minerals and other contaminants into the sea (Chandrasekhar, et. al., 2003). Pazhayakayal influenced by the Thamirabarni estuary south of Tuticorin harbour forms a dumping ground for point and non-point source of Contaminants. Similarly, Hare Island near Tuticorin harbour and Kallar river confluence are important places in Tuticorin coast, which are under stress.

Physiographically, the coastal stretch of Tuticorin is falt and narrow Islands such as Pandyan Tivu, Kosuwari Tivu, Kariyashuli Tivu and Van Tive are present within five km distance from the Coast line, afford protection from wave action and erosion. The backshores of this Coastal segment comprise of Salt pans. The Vaippar and Kallar River confluence located in the Gulf of Mannar near Sippikulam. These two rivers form the estuarine system in the northern part of Tuticorin harbour. The coastal segment between Sippikulam and Naripariyur is open without any offshore islands or salt marsh plants and is exposed to direct wave action. The coast line near Kannirajapuram is found to have large extent of beach rocks. Wide and flat sandy beaches with numerous sand dunes covered with salt marshes are seen near mukkaiyur- Gundar river joins the sea near Mukkaiyur. The beaches between Mukkaiyur and Valinokkam are very wide with elevated dunes. A bay formation has been identified on the northern part of Valinokkam. Kallar is an extension of Malatta Odai and form's an estuarine system. Between Kallar and Tuticorin the beach is wide with many sand sheets. Korampallam creek starts from its pond and joins Gulf of Mannar near Tuticorin Harbour. River Thamiraparani forms a broad estuary near Pazlayakayal in the southern part of Tuticorin harbour. This estuary extends from 8^0 25' 12" to 8^0 40' 10" N and 78^0 3' 90" to 78^0 10' 26" E, being Connected to sea at three different positions. 8^0 36' 50" N to 78^0 8' W, 8^0 38' 4" N to 78^0 8' W, and 8^0 40' 09" N to 78^0 8' W **(Figure 1).**

2.1 Site 1

It is located at Kallar estuary off Tuticorin Coast near Gulf of Mannar, extending towards Vaippar. It is bound to the north by Vaippar River, to the south by the major industrial centre, Tuticorin. The estuary is dry during major part of the year due to lack of fresh water inflow, sea water intrusion occurs to the inland, rendering high salinity. This Site extend, from 80 57'. 13" to 8^0 57' 22" N and 78^0 11'50" to 78^0 12' 33". This Site is located away from the industries.

2.2 Site II

Site II is located in a relatively open coast marked by Karapad Creek, Where mangrove vegetation forms very dense strands **(Photo.1)**. It is extended to all sides by major industries such as southern petrochemical Industries Corporation Pvt.Ltd., Thermal Power Plant, Spinning Mill, etc. Besides, the mangrove Stands form a major dumping ground for municipal waste and sewage disposal. This Site stretches from 80 44' 59" to 8^0 47' 16" N and 78^0 09' 45" to 78^0 09' 36" E.

2.3 Site III

This Site is situated at Pazhayakayal estuary off Tuticorin coast near Gulf of Mannar. It is bound by Tuticorin harbour in the north and the Dharangadara Chemical Works in the South. Towards the east is situated the boat- yard and salt pans towards the west. It is falling within the latitudes 8^0 40' to 80 35' N and Longitudes $78^0$10' to 78^0 13'E.

III. Material and methods

3.1 Sample Collection

Mangrove water and sediments, and groundwater samples were collected from different locations in three Sites including Kallar estuary, Tuticorin creek and Pazhayakayal estuary. Sampling points were limited to ten for surface water, sediment collection and groundwater collection. The periodicity of sampling was seasonal i.e pre-monsoon (April 2005 to June 2005) and post monsoon (February 2006 to April, 2006). Water Samples in duplicates for the measurement of various inorganic and organic constituents, were collected in pre-Cleaned, oven-dried (45^0C over night) polyethylene bottles. Immediately after collection, they were Stored in an ice box and brought to the laboratory and filtered through 0.45µ membrane into acid washed bottles and stored in refrigeratior for immediate analysis using standard methods. Special care was taken in the case of estimation of dissolved oxygen, where the samples are collected in 300ml acid washed reagent bottles and fixed immediately to avoid contamination. Water Samples used for determination of metals were acidified to pH 2 by adding of 10M HCL. The Second duplicates was kept at its natural pH and used for analysis of other physico-chemical parameters. The sediment Samples of root zone were collected by using Van veen Grab sampler. The Collected Samples were first air dried and then dried in the hot air oven at 90^0C. The Samples were preserved in thick polythene bags and labeled for further physio-chemical analysis using standard methods.

3.2 laboratory methods

The collected mangrove water and groundwater samples were filtered and acidified with nitric acid for analysis. The samples were analysed for concentrations of major components namely calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K), carbonate (CO_3), bicarbonate (HCO_3), chloride (Cl) and sulphate (SO_4) and minor elements. The analytical procedures used are according to APHA (1984) and the methods adopted are given in **Table.1.** During the analytical procedures, blanks and standards were run to check the reliability of the methods adopted. After completion of the analysis of major ions the ion balance error was calculated. In general ion balance error was within 10%.

Parameters	Methods
Ca^{2+} and Mg^{2+}	Titration using 0.05N EDTA
Na^+ and K^+	Flame Photometer
HCO_3^- and $CO^2{}_3^-$	Titration using 0.01N H_2SO_4
Cl^-	Titration using 0.05N $AgNO_3$
SO_4^-	Turbidity
Heavy metals	AAS

Table.1 Methods are used in analysis of water samples

3.3 Textural Analysis

Textural Analysis of the Sediments were Carried out by the method of dry sieving after taking known quantity of Sample. The dry sieving was made at 1/49 (phi) interval for the size range from 2500 to 63 µm using a mechanical Ro-Tap sieve shaker for 15 minutes (Folk, 1974) Size range less than 63 µm was separated by pipette method (Krumbein and Pettijohn, 1938) by Collection of Specific volume of the Suspension from a specific depth, following decantation method. Clay particles were tabulated. The valves were fed into the ternary diagram (Shepard 1954) for granulometric classification of sediments. Statistical parameters such as mean size (m_2), Standard deviation (σ)Skewiness (SK), Kurtosis (Ka) were Calculated by following the procedures of folk and word's (1957) formula.

3.4 Organic carbon

Organic Carbon (Walkley-Black, 1934; and Elwakeel and Riley, 1957); modified by gaudette, etal., (1974). About 0.5 gram of powdered sediments sample was oxidized woth 10ml of 1N potassium dich roamate solution in an exlenmeyer flask and 20ml of Con. H2So4 was added gradually and keep aside for half an hour with occasional shaking. Then it is added with 200ml of distilled water, 10ml of phosphoric acid, 0.2g of dry sodium fluoride and titrated against standard ferrous amnium sulphate (o.5N) using 1ml of diphenylamine as indicator. At the end point the dull green colour changed into turbid blue to brilliant green clolur. A blank experiement was conducted under the same conditions using distilled water. The percentage organic carbon was claulated as follows.

$$\% C + 10(1-T/s)$$

where

T = volum of terrous ammonium sulphate consument by sample.
S = Valum of ferrous ammonium sulphate consumed by blank.
OC = Organic carbon.

3.5 Carbonate (Hutchinson And mar Lennan's Method, (1947)

Carborate in the sediment samples was determined by the Hutchinson and flax Lennan's method (1914) by neighing out exactly 0.5g of the powdered sample taken in a breaker followed effervescence cased, 20ml of the supernatant solution was with drown and titrated against standard sodium hydroxide solution using bromothymod blue indicator. A blank titration was also perform under the same conditions and the percentage of carbonate in the sample was calculated as %CO_3 = (T-s)10 where, T is the titre value for the first titration, S being the value for 2.5 freparation of water Exact from Aquatic sediment.

The most common method for analyizing physoico – chemical parameters in sediments involves the use of extraction of the sediment sample with water. The concept of extraction components/ elements in the sediments in the sediments is brought into the liquid phase using water as the medium. This procedure involves two or three step sequential extraction for the analysis of pH, Eh, alkalinity, salinity and nutrients in the sediments. 100 gram of air dried sediment was taken in 500ml beaker and stirred well for 30 minutes and allowed it to stand for few minutes. This extract was used for determination of Ph, Eh and Ec as the methods prescribed for water sample below.

3.6 Physico – Chemical Characteristics of Mangrove Water

The physico-chemical composition of marine sediments and water can provide important information regarding the origin and composition of sediment, water quality and role of mangrove to control this process. The influx and distribution of heavy metals both in the abiotic and biotic compartments individually and between compartments are also affected by parameters such as rainfall, pH, dissolved oxygen and salinity. In turn, the physio-chemical features determine the fate of components input through biological processors, atmospheric and terrestrial process and digenetic reaction taking place in the mangrove system.

Continental margins associated with mangroves are again as important as the deep sea in terms of the biogeochemical cycling of carbon and nitrogen, although they account only 20% of the surface area of the world oceans (Walsh, et al., 1991). The supply of plant nutrients is of particular importance for the quality of mangrove water. Increase in nutrient supply results in enrichment of primary productivity and accumulation of biomass, with secondary effects resulting in changes in plank tonic community structure (Smetacek, 1985). In view of the importance of the environmental parameters, in the present study also, data on the general physio-chemical parameters are observed and studied seasonally and an attempt is made to understand the relationship between these parameters.

3.6.1 pH

pH of marine water is relatively constant, and in controlled by bicarbonate ions, which is the major inorganic carbon species present in the water (Mason and Moore, 1982). The spatial and temporal variation in pH for the study area is presented in Table 6.1.

The study area seems to have high buffering capacity as a result of which only marginal changes in pH has been recorded. It ranges from 7.1 to 8.74 throughout the study period. The minimum average (7-8) is recorded during monsoon season at Site II could be due to increase in flow of domestic sewage near the sampling location. Similar trend at Sites I and II is also due to more fresh water flow from the rivers such as Kallar and Thamiraparani.

3.6.2 Dissolved Oxygen (DO)

The quantity of dissolved oxygen in mangrove ecosystem determines its productivity by controlling various diagenetic reactions taking place in water medium. The DO in the study period (Table 6.1) varied from 0.635 to 5.23 mgl^{-1} indicating polluted nature of the environment, as the DO is an index of physical and biological processes operating in water. The minimum average value of 1.240 mgl^{-1} during post monsoons season at Site II might be due to combined effect of photosynthetic activity of producers and biochemical oxidation of untreated waste entering the marine environment. The higher average valve of DO reported at Site III during per monsoon (4.36mgl^{-1}) could be the effect of higher solubility of oxygen in low saline water **(Table.2)**. Similar reports have been made by various authors showing that the solubility of oxygen decreases with increasing salinity and temperature (Gouda and Panigraphy, 1989, Das, et al., 1997). This also account for comparatively less dissolved oxygen in Site I during pre and post monsoon seasons. The negative correlation between DO and salinity during pre monsoon season is an evidence for low solubility of oxygen at high salt concentration.

3.6.3 Salinity

Salinity of shoreline habitat is controlled by climate, hydrology, topography an tidal flooding (Twilley and Chen, 1998). The spatial and temporal variation of salinity is presented in table.2. In general the salinity is found to be high in premonsoon seasons especially at Site I and III. This is mainly due to minimum influx of fresh water resulting in maximum interference of marine environment. Also the productive salt industries associated with these areas cause intrusion of salt bitterns in to the study area. Salinity shows significant positive correlation with Eh and EC that suggests its role in controlling these parameters. Its negative correlation with many metals indicates desorption of heavy metals in the saline environments.

3.6.4 Alkalinity

Alkalinity in seawater refers to the presence of basic salts of sodium and potassium in addition to calcium and magnesium. This study shows both seasonal and spatial variation. Alkalinity showed an inverse relationship with salinity. The high concentration of alkalinity during monsoon season (the average values range between 67.5mgl^{-1}) is attributed to the contamination by leaching process through surface water during rainy season. On the other hand during post monsoon its average valves range from 398 mg1^{-1} to 63-25 mg1^{-1}.

3.6.5 Major ions

The distribution of Ca shows its maximum average values (64.6 mgl^{-1}) at Site III during post monsoon that indicates replacement of Ca^{++} on the clay surface by most abundant Mg^{++} under saline conditions resulting into diffusion to the overlying water column. In the present investigation, magnesium is found to be in higher concentration compared to calcium (**Table 3**). Higher average of 348.5, 314 and 313.5 mgl^{-1} for Site I, II and III respectively during post monsoon was recorded. This increase in concentration of magnesium during this season is an indication of salt water intrusion, as sea water is known to be enriched in magnesium than calcium (David and De Wiest, 1966). Calcium shows positive correlation with Si in all the seasons Tables 8.4 to 8.6 and with salinity in pre monsoon indicates the detrital origin and diffusion into the water column under saline condition.

In coastal water of Tuticorin impacted by industries, sodium and potassium are about 2476 ppm and 198 ppm respectively. This higher concentration of sodium during pre monsoon and post monsoon is attributed either due to evaporation and lack of fresh water inflow or due to sea water intrusion. Concentration of potassium is lower than sodium in the study area. The lower value of potassium rather than sodium was due to greater resistance of weathering of potassium and its fixation in the formation of clay minerals. And further it indicates its origin from remineralisation of dead mangrove foliage.

3.7 Heavy metals in salt marsh water

Mangrove sediments are a potential source of heavy metals to overlying water because they eventually receive almost all the heavy metals, entering the aquatic environment. Far from being static sink of these substances, it moved and reworked by various physical, chemical and biological processes, result into higher metal remobilization to the water column. Also, the bio-geo-chemical processes occurring at the water sediment interface will keep trace metal constantly cycling among the coastal compartments, resulting in comparatively higher concentrations of trace metals in coastal waters as compartments, resulting in comparatively higher concentrations of trace metals in coastal waters as compared to adjacent sea or river waters.

3.7.1 Distribution of Fe, Mn, Cu and Pb

Iron in this study shows uniform distribution except Site III, where considerably higher concentration of iron is noted. At this Site there is also a maximum in the amount of organic carbon in the sediment, suggesting that iron in the form of organic probably humic complexes leached out of the sediment.

Mn exhibits its maximum leachability under reduced condition from the sediment to water surface. The significantly positive correlation between Fe and Mn ($r = 0.81$ in post monsoon and $r = 0.981$ in post monsoon and $r = 0.645$ in monsoon) confirms the behaviour of these metals which is similar with respect to their redox sensitivity. It is also suggested that in post monsoon season at Site III concentration of dissolved oxygen (DO) is more. So it is possible that the oxidized mangrove environment can cause oxidation of Mn thereby scavenging the other trace metals too. This is the case for the Site II samples where very low Eh and DO cause mobilization of manganese to the water column.

Cu shows positive correlation with different metals at different metals at different season. Its weak correlation with iron, aluminium and Si indicates the anthoropogenic origin of the metal in the present study, though it is a metal of weathering products. In the study area the average concentration of lead ranges between 0.2 mg/L and 0.312 mg/L during premonsoon season, 0.207 and 0.415 mg/L during post monsoon season and 0.17 and 0.415 mg/L during post monsoon season. Strong influence of atmospheric inputs of fly ash from near by Thermal power Plant might be responsible for lead concentration in the Site II (**Table 4**).

3.7.2 Distribution of Zn, Cd, Ni, Cr and Hg

In the study area the mean concentration of zinc varies from 0.066 to0.495 mg1^{-1} during pre monsoon and 0.072 to 0.462 during post monsoon period. These are remarkably higher than what were reported earlier from the

Tuticorin Bay, but lie within the range reported from the estuaries and other coastal compartments (0.01 to 6.2 $mg1^{-1}$.

Concentration of cadmium in the present study is much higher than the amount reported in other parts of the world. Season wise distinction is obvious. In the premonsoon, the average concentration ranges from 0.05 t 0.085 mgl^{-1} and in the monsoon the concentration being much higher (0.102 to 0.16 mgl^{-1}). In the post monsoon season, it ranges from 0.05 to 0.305 mgl^{-1}. The elevated level (1.00 mgl^{-1}) at some sites as Site I and II during post monsoon is associated to high degree of industrialization.

Nickel in the study area is widely distributed and far exceeding the natural background level (0.002 mgl^{-1}) (Dickenson, 1974a). The concentration throughout the study period ranges between 0.01 mgl^{-1} and 0.31 mgl^{-1}. Chromium has no consequences in water as it concentration in the study is around the safe level limit. In salt marsh water, the concentration of metal is very low (0.0003 ppm) due to the high affinity of mercury for sulphur groups resulting in strong immobilization from the sediment.

3.8 Microbial contamination

Bacterial and fungi population present in water environment reveals the nutrients inpt of the site. In the present study, all sites have considerable amount of bacterial and fungi population. DOC and organic carbon concentraio of the mangrove water supporting the population growth in the study area. Presence of total coliforms indicates the antropogenic input through Rivers and other sources. Especially high concentration of total coliforms in the site III show high input of anthropogenic in put in this area through Thamparabarani **(Figure.2)**.

IV. GROUNDWATER HYDROCHEMICAL STUDIES

Groundwater hydrochemical study is necessary to comprehend the quality and pollution status of a groundwater environment. Such a hydrochemical study was carried to determine the concentration of major ions, trace elements and microbial, identify the hydrochemical patterns and to assess the pollution status of groundwater of the study area. The groundwater of the study area is generally colourless and odourless. The temperature of the groundwater varies from 30^0-35^0 C. In this chapter, groundwater hydrochemical distribution and the hydrochemical water types are discussed.

4.1 Hydrogeochemistry

4.1.1 EC and pH

The most common in situ water tests such as EC and pH provide useful preliminary information about a system together with water quality information. In the study area, the EC (electrical conductivity) of the groundwater samples varies from 454 to 1360 μS/cm. The pH generally varies from 7.2 to 7.8. Not much variation was seen in the between the two seasons (Pre and post monsson). However, concentration of ions was more during post monsoon season compared to pre-monsoon may be due to dissolution. Site specifically, The Site I and Site II are having less concentration of ions compared to Site II that is Pazhayakayal.

4.1.2 Major ions chemistry

Major ions are the primary constituents of groundwater, which fix the quality of groundwater at most of the time at any place. Study of major ion concentration of the groundwater will provide general information about the quality status of an aquifer system. The ranges of concentration of major ions in groundwater of the study area are given in **Figure.3**. The concentrations of dissolved major cations and anions in the groundwater vary both regionally and seasonally. Abundance of these ions is in the following order:

$Ma>Ca>Na>K=HCO_3>Cl>SO_4>CO_3$.

4.1.3 Seasonal variation

In general, hydrochemistry of groundwater of any place varies seasonally and regionally according to groundwater recharge, discharge and geochemical reactions in the aquifer. Here in the study area, seasonal variation of the groundwater chemistry for the period of pre monsoon 2005 and post monsoon 2006 (**Figure.3 and 4**) shows increasing pattern. Seasonal variations in the major ion chemistry of the wells located in Pazhayakayal shows huge increase (**Figure.3 and 4**) may be due to dissolution contaminants during rain fall. Similarly, Site I and Site two also show slight increment in concentration.

4.1.4 Regional Variation

Regionally, major ion concentrations of groundwater of the study area vary according to recharge, landuse pattern. Calcium values range from 30 to 90 mg/l and is the dominant cation of the study area. Groundwater from wells located in Site III has high concentration of calcium. The maximum concentration of calcium is found in the Site III. The minimum and maximum value of magnesium ranges from 80 to 160 mg/l. The maximum concentration of magnesium is found in the Site III of the study area. There is not much variation in the concentration of the magnesium ion of the groundwater samples in the wells located in the Site I and Site II. The sodium concentration of the study area varies from 30 to 160 mg/l and potassium values range from 5 to 80 mg/l. Maximum concentration of the potassium is observed in the well no: 21. High concentration of sodium and relatively low concentration of potassium in the groundwater might be due to the weathering of silicates. They have reported that it may be due to the resistance in weathering or fixation of clay.

The minimum and maximum concentration of HCO_3 ranges from 150 to 360 mg/l. Maximum concentrations of bicarbonate are found in the Site III of the study area and along the river banks **(Figure.3).** High concentration of bicarbonate in groundwater might be due to the weathering of silicate rocks and dissolution of carbonate precipitates and the recharge of rainwater.

Carbonate concentration in groundwater of the study area ranges from 0 to 60 mg/l. Chloride content ranges from 60 to 240 mg/l. The western part of the study area, where Site III is present has the maximum concentration of chloride ion. The chloride concentration of groundwater of the wells located in alluvial formations is higher than that of the wells located in the hard rock formations. Sulphate concentration is very low and it ranges from 5 to 20 mg/l. Groundwater of Gondwana clay region has more amounts of dissolved ions than other parts may be due to the dissolution of precipitates and clay material.

V. HYDROCHEMICAL FACIES

The Piper trilinear plot, prepared with the hydrochemical results of groundwater collected from the study sites, clearly indicates the hydrochemical facies (**Figure.5**). Four major hydrochemical facies have been identified based on the major ion chemistry of groundwater of this area. They are:

i) Ca-Mg-HCO_3 facies
ii) Na-Mg-Cl facies
iii) NaCl

The Ca-Mg-HCO_3 and Na-Mg-Cl facies are dominant in this region. Ca-Mg-HCO_3 is present in the Site I and II. This type of water might have been derived from recharge waters. The Na-Mg-Cl facies of groundwater is generally present in the Site III, which might have been derived from reverse ion exchange. The Na-Cl facies is found in the groundwater samples occurring in the few wells of Site III as a small patch near the river where a small contaminant pond is found. There is no difference in the distribution of various hydrochemical facies between the groundwater of Site I and II.

VI. Heavy metals

As the study area is an industial region, it has huge possibility of heavy metal contamination. So the groundwater samples were tested for heavy metals. The concentration of heavy metals in groundwater varies from 0.5 –2 mg/l. Regionally heavy metals concentration varies according to the geology and presence of industry. Near Tambarabarani River confluence that is Site III. Generally heavy metal concentration of the groundwater is in safe limits.

VII. Groundwater quality variations

7.1 Hardness

The groundwater of the study area is slightly alkaline. The alkalinity expressed as $CaCO_3$ ranges between 130 and 388 mg/l. The hardness of water attributed to the Ca and Mg ions dissolved in the groundwater varies between soft and hard water. The classifications of groundwater based on hardness (Matthess 1982) of representative wells are presented in the **Table.5.**

Hardness classification	Hardness as $CaCO_3$ (mg/l)	Well Nos. Pre-monsoon	Well Nos. Post monsoon
Very Soft	0-50		
Soft	50-150	Site I and II	
Average	150-250	Site III	Site I
Hard	250-500		Site II and III
Very Hard	>500		

Table.5 Classification of groundwater based on hardness

7.2 Irrigation water quality

The groundwater of the study area is mainly used for irrigation purpose. The suitability of the groundwater for irrigation mainly depends on the minerals dissolved in it. These dissolved minerals may not affect plant growth directly but it will change the chemical and physical nature of the soil. So water used for irrigation must have some standard amount of dissolved minerals, using exempted water will affect the plant growth. Water quality constraints for irrigation can be tested by different empirical indices established by various researchers through field knowledge and experiments.

The electrical conductivity of water will affect the the root zone and water flow, because it is directly related to the osmotic pressure. Relation between EC and (ms/cm) and osmotic pressure (OP in atmospheres) given by Lloyed and Heathcote (1985) is,

$OP = 0.36 \times EC$

According to the United States Salinity Laboratory’s Guide (USSL, 1954) groupings of irrigation water, Site III is not as good as for irrigation purpose. All others wells are falling in permissible and good for irrigation. Similarly, high sodium in irrigation water will be exchanged to soil for Ca and Mg, leading to soil alkalinity. This effect significantly reduces soil permeability and decreases crop yield. Hence, sodium absorption ratio was calculated and plotted against EC in the USSL proposed diagram **(Figure.5).** In this diagram, few wells are exceeding the limit.

Carbonate dissolution and deposition also cause problem for irrigation. Hence, an index known as Residual Sodium Carbonate (RSC) is used to know the tendency of calcium to precipitate in the soil which increases the relative sodium concentration and exchangeable sodium percentage. The groundwater of the study is classified based on RSC which is calculated using the following relation,

$RSC = (CO_3 + HCO_3) – (Ca + Mg)$

The concentration is expressed in milliequivalents per litre of water. If RSC (meq/l) value of water is less than 1.25, it is safe for most purposes. If it is between 1.25-2.5 means marginal water or if it is greater than 2.5 means not suitable for irrigation. In general, groundwater of the study area has less than 2.5 meq/l, hence they are marginal to safe water with respect to bicarbonates.

7.3 SOURCES FOR MAJOR IONS

Major ions present in the groundwater of the study area might have come from different sources. Hydrochemical studies will give us preliminary information about the sources of these elements. High concentration of magnesium and bicarbonate might have been come from carbonate weathering. High sodium ion concentration might be due to silicate weathering and influence of the estuary **(Figure.6).** Increased concentration of chloride might be due to river water input, irrigation return flow, high residence time and other anthropogenic activity in the estuary. Low concentration of potassium may be due to its greater resistance to weathering and its fixation in the formation of clay minerals as reported by Mohan et al (2000). Similarly, low concentration of sulphate may be due to lack of source for it or due to reduction process. Classification of water types also gives us an idea about the sources. The Ca-Mg-HCO_3 and Na-Mg-Cl facies are dominant in this region. These type waters might have been derived from recharge waters and reverse ion exchange. The Na-Cl facies is found in the groundwater samples occurring in a small patch near the river Thamparabarani. This might be derived from anthropogenic activity and recharge from a contaminant estuary of Thamparabarani. The above study reveals that hydrochemical processes, river water input, irrigation return flow and influence of contaminated marine water might have contributed more ions to groundwater.

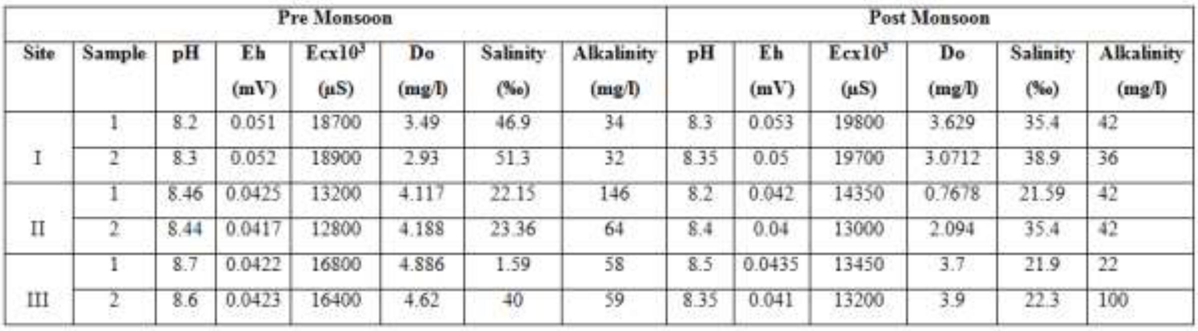
VIII. CONCLUSION

Violent hydrodynamic conditions was present in Kallar and Pazhayakayal and receiving high fluvial input from inland, hence water and sediment of this sits are having high amount of organic carbon, heavy metals and microbials. Salinity is comparatively low in post monsoon due to high inflex of fresh water.

Near Tuticorin horbour concentration of heavy metals are high due to harbour activities. In Kallar and Pazhayakayal mangrove water heavy metal concentration is comparatively lower. However, lead concentration is more in Pazhayakayal due to fly ash deposition from thermal plant.

Over all mangrove environments in the all three study sites are highly affected due to industrialization and anthropogenic activity. Groundwater samples collected along the coast in all the three sites are not much affected by the contaminated marine water. The Ca-Mg-HCO_3 and Na-Mg-Cl facies are dominant in this study sites. These type waters might have been derived from recharge waters and reverse ion exchange. The Na-Cl facies also found in a small patch near the river Thamparabarani. This might be derived from anthropogenic activity and recharge from a contaminant estuary of Thamparabarani. The above study reveals that hydrochemical processes, river water input, irrigation return flow and influence of contaminated marine water might have contributed more ions to groundwater. However, the groundwater is not much affected in all the three sites.

People are considering the laws and policies after major out breaks happened to the environment. An at least now serious step has to be taken to protect the mangrove environment along the Tuticorin coast. This may improve the mangrove environment, marine organisums, as well as the coastal aquifer system.



		Pre Monsoon						Post Monsoon					
Site	Sample	pH	Eh (mV)	Ecx10^3 (µS)	Do (mg/l)	Salinity (‰)	Alkalinity (mg/l)	pH	Eh (mV)	Ecx10^3 (µS)	Do (mg/l)	Salinity (‰)	Alkalinity (mg/l)
I	1	8.2	0.051	18700	3.49	46.9	34	8.3	0.053	19800	3.629	35.4	42
	2	8.3	0.052	18900	2.93	51.3	32	8.35	0.05	19700	3.0712	38.9	36
II	1	8.46	0.0425	13200	4.117	22.15	146	8.2	0.042	14350	0.7678	21.59	42
	2	8.44	0.0417	12800	4.188	23.36	64	8.4	0.04	13000	2.094	35.4	42
III	1	8.7	0.0422	16800	4.886	1.59	58	8.5	0.0435	13450	3.7	21.9	22
	2	8.6	0.0423	16400	4.62	40	59	8.35	0.041	13200	3.9	22.3	100

Table.2 Physical Parameters of Salt marsh Water at Different Seasons

Site	Sample	Fe	Mn	CU	Pb	Zn	Cd	Cr	Co	Hg	Ni	As
I	Average	0.019	0.012	0.158	0.213	0.495	0.050	0.021	0.038	19.00	0.063	2.295
II	Average	0.020	0.009	0.345	0.313	0.320	0.085	0.024	0.146	49.000	0.113	1.253
III	Average	0.030	0.061	0.190	0.066	0.066	0.060	0.018	0.098	346.500	0.058	1.425

Table.3 Concentration of Heavy Metals (mg/L) in Salt Marsh Water – Pre Monsoon

Site	Sample	Fe	Mn	CU	Pb	Zn	Cd	Cr	Co	Hg	Ni	As
I	Average	0.023	0.012	0.16	0.195	0.073	0.053	0.012	0.015	23.75	0.058	1.738
II	Average	0.023	0.008	0.368	0.418	0.085	0.305	0.021	0.165	163.000	0.178	1.095
III	Average	0.034	0.010	0.228	0.173	0.463	0.098	0.021	0.143	377.250	0.085	1.205

Table.4 Concentration of Heavy Metals (mg/L) in Salt Marsh Water Post Monsoon

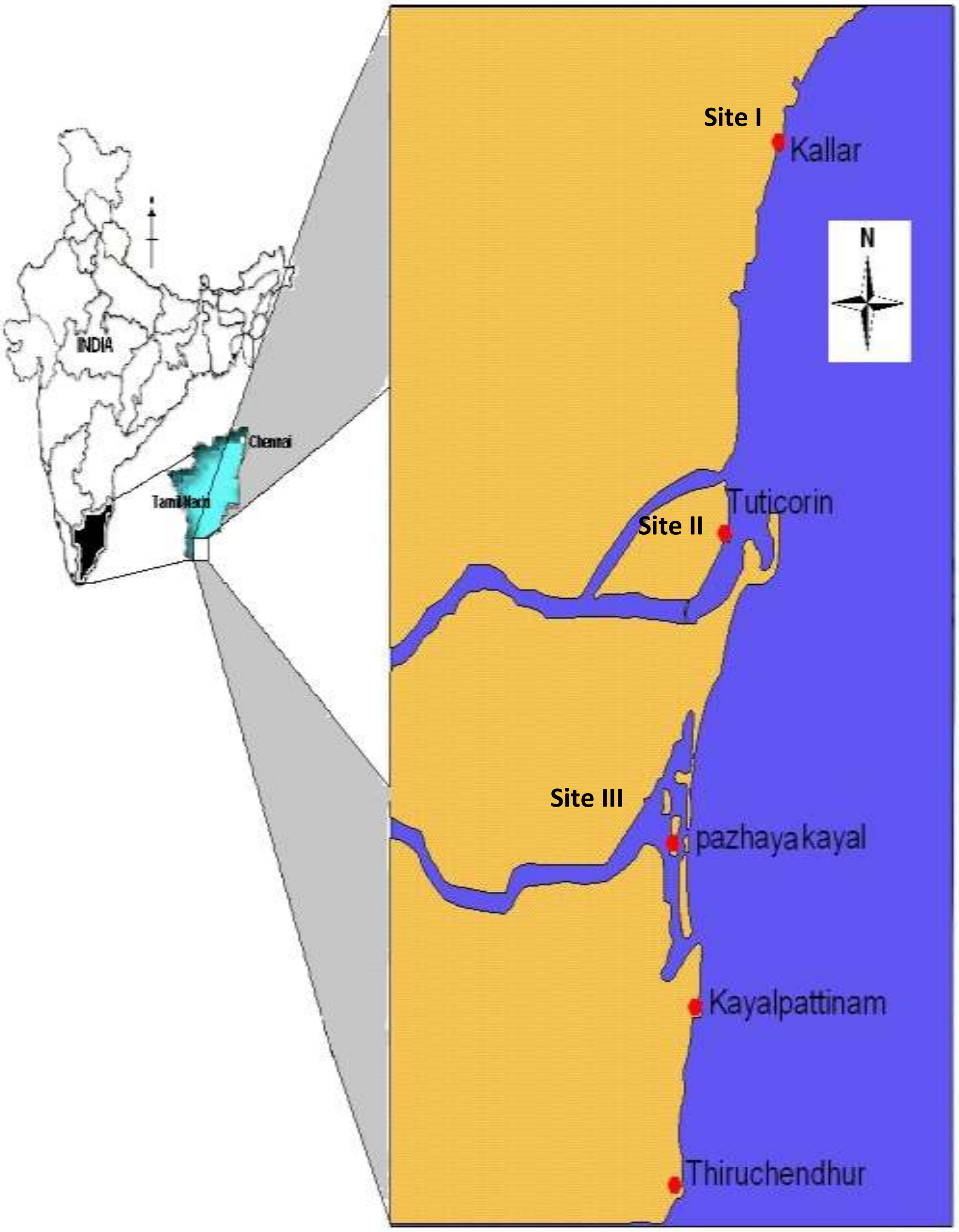


Figure.1 Location map of study area

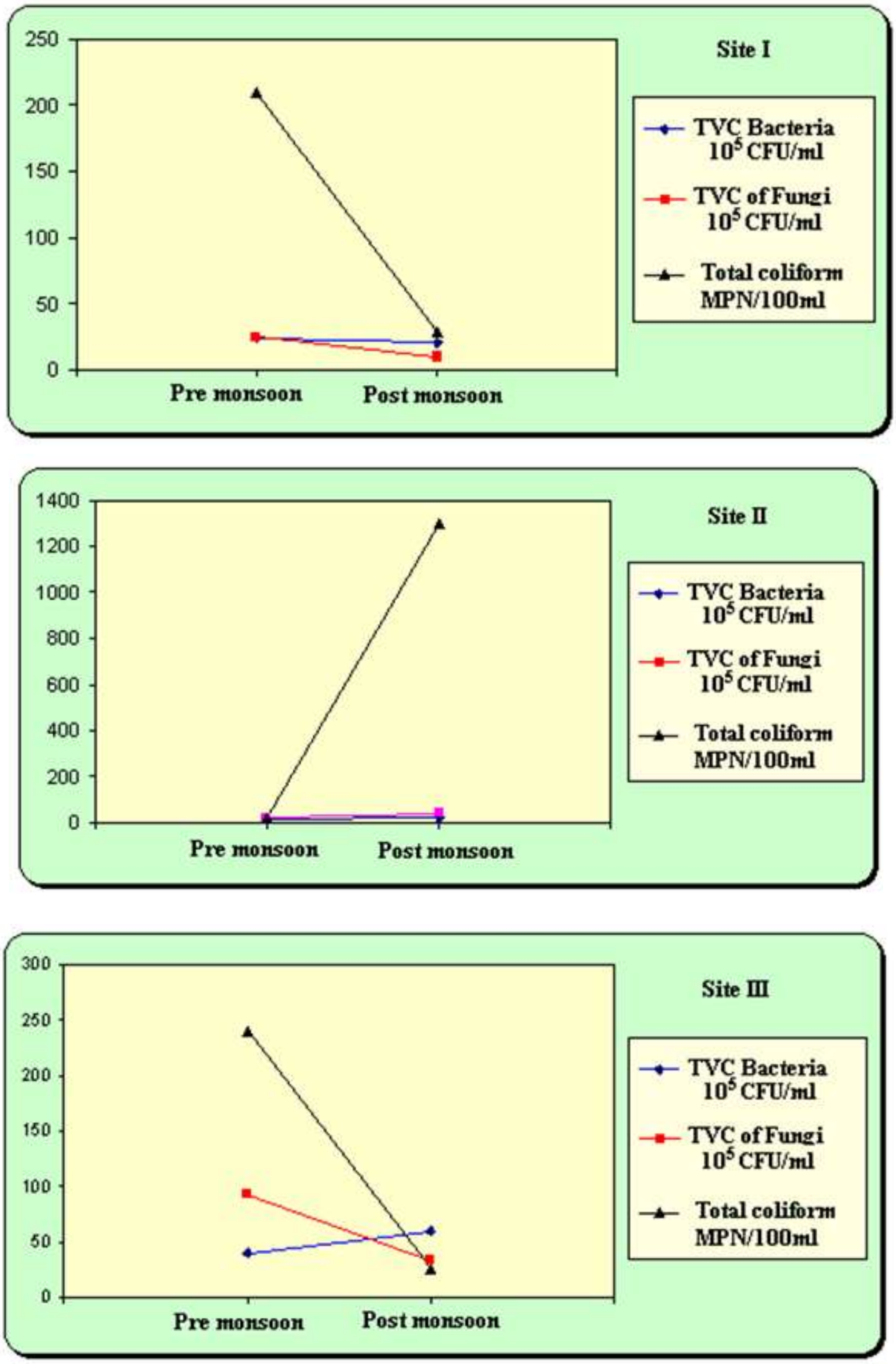


Figure.2 Microbial concentration of mangrove water in season wise

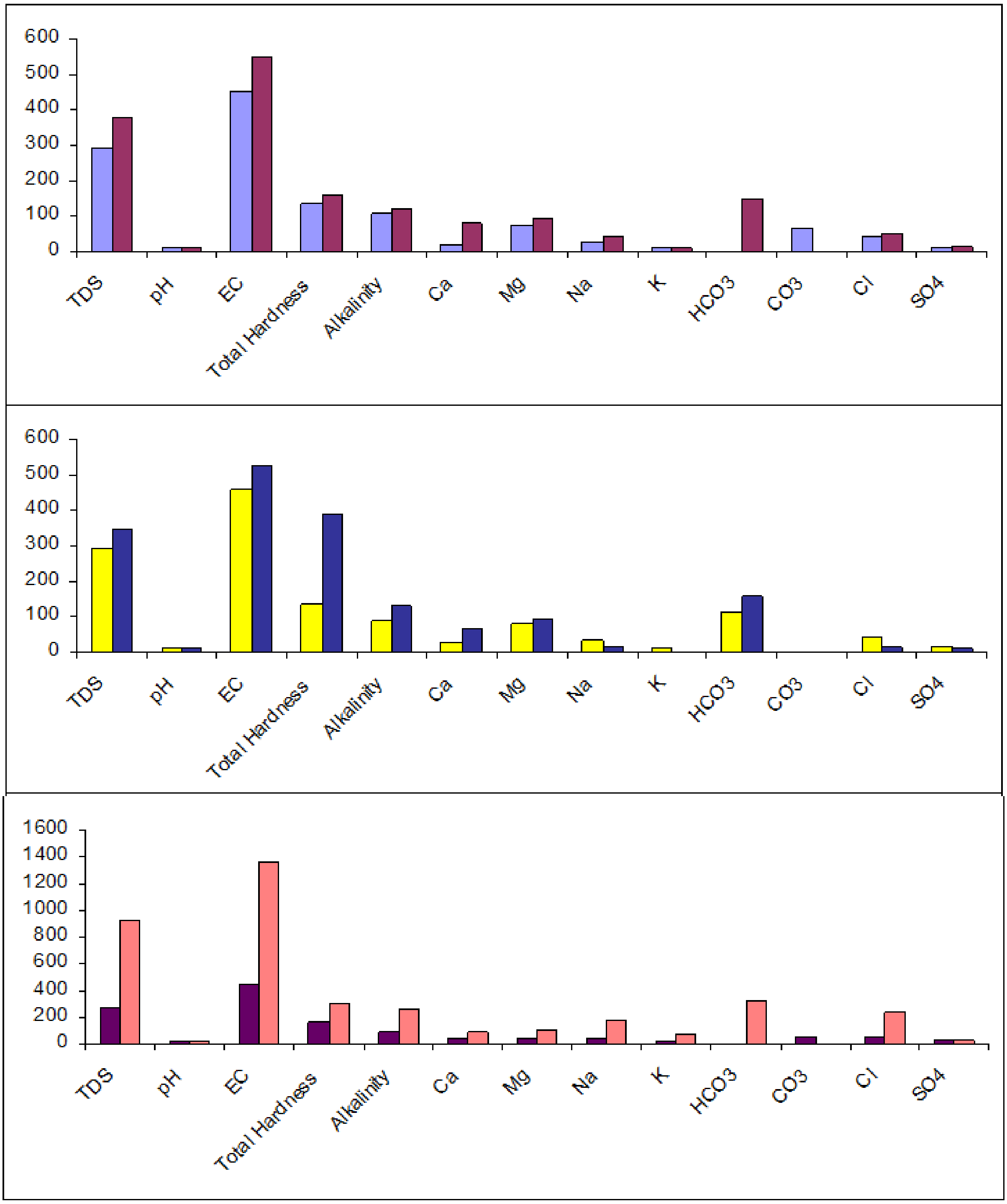


Figure.3 Concentration of ions and other properties of Site I Site II and Site III

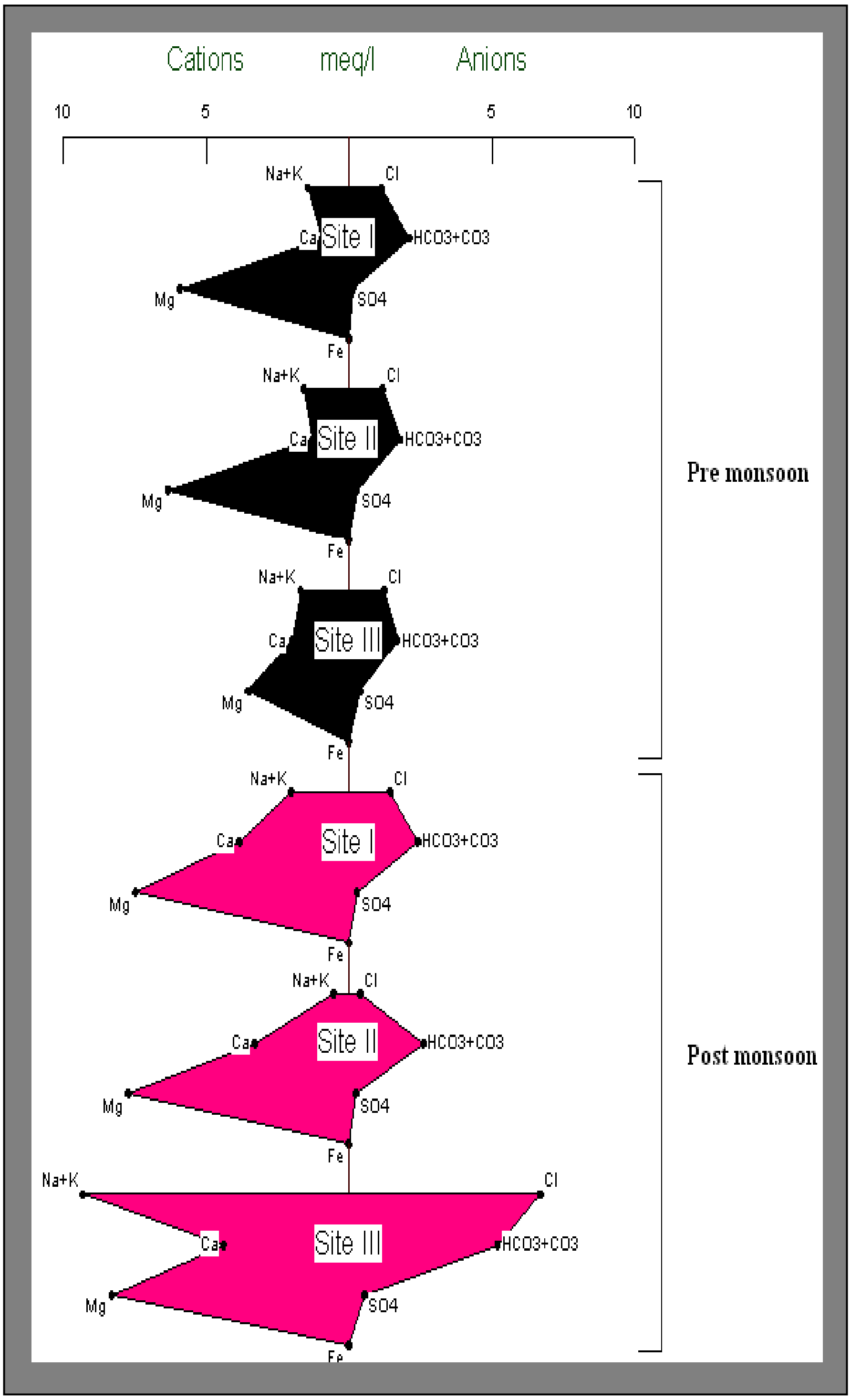


Figure.4 Concentration of major ions in the study area

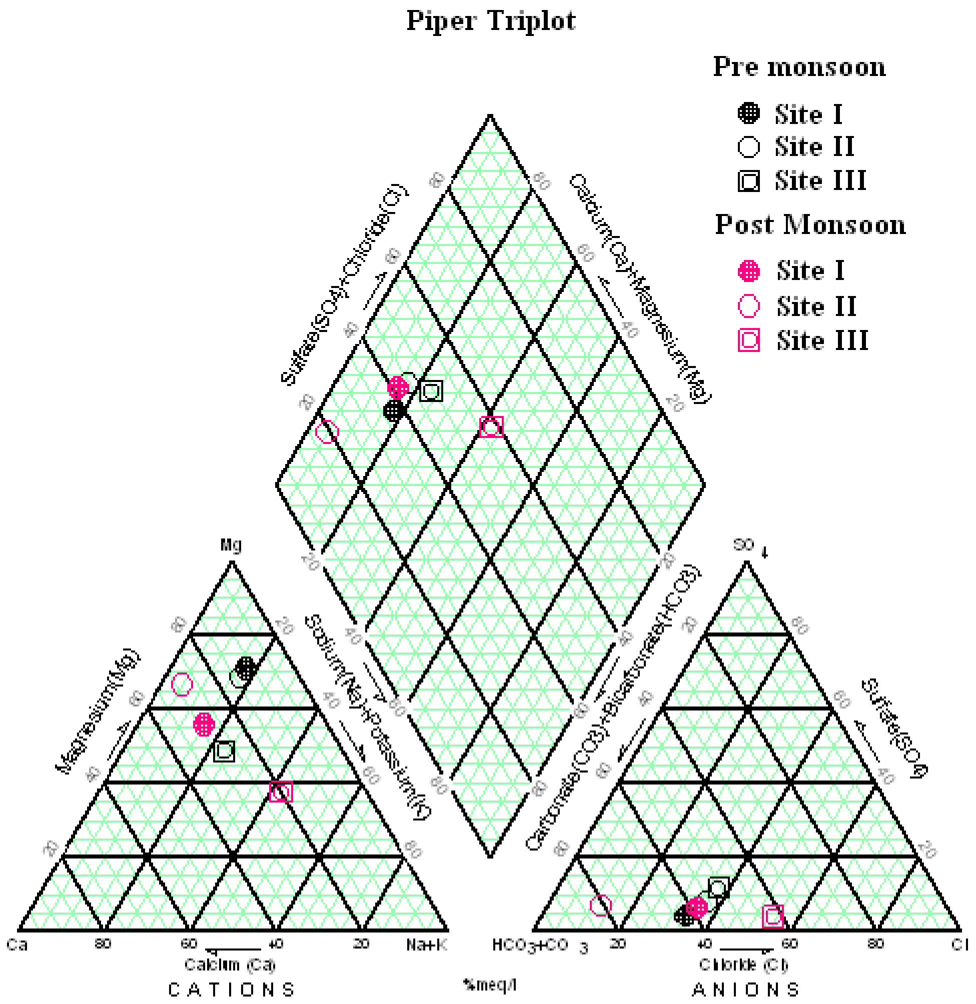


Figure.5 Piper triplot of groundwater samples

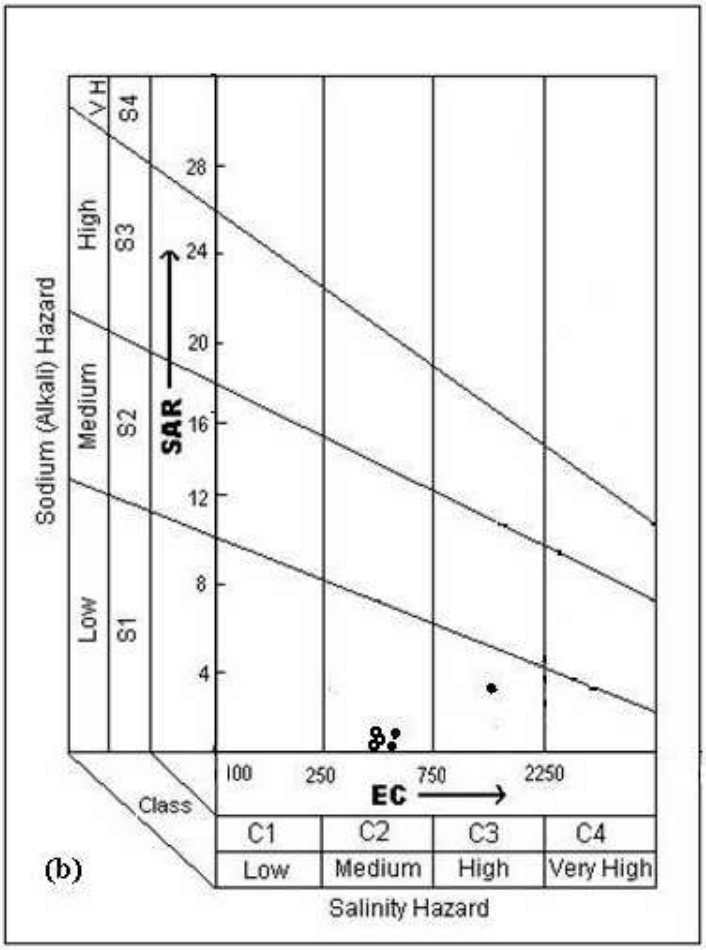
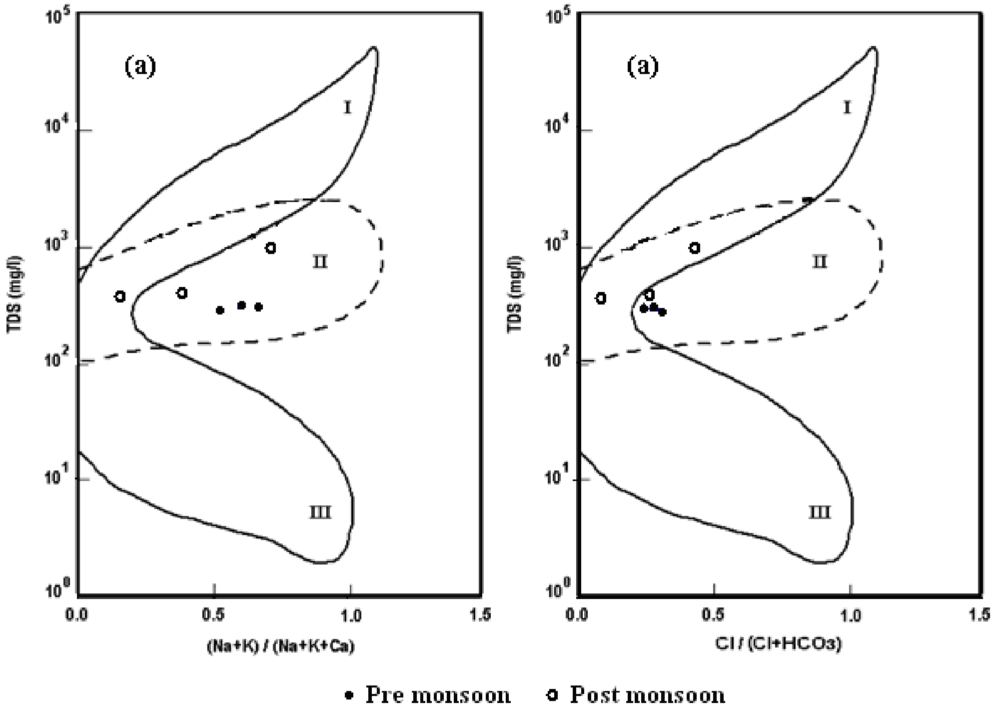


Figure.6 Salinity and SAR classification for irrigation water use



I Evaporation, II Rock water interaction and III

Figure.7 Classification of water type along the study area

Photo.1 Dense mangroves along the study area

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