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Preliminary Study on the Decadal Changes in Temperature and Rainfall on the Hydrochemistry of Surface and Groundwater in Coleroon River Estuarine Zone, East Coast of India

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Abstract: Estuaries are zones of interaction and transition between groundwater and the sea where dissolved constituents like pollutants, nutrients, etc. can be diluted, exchanged, transformed and consumed. An attempt has been made in the Coleroon river estuary, India by hydrochemical evaluation, ionic ratios and nutrient flux to characterize the submarine groundwater discharge with respect to climate change. Selected ground water and surface water samples were collected during two different seasons and analyzed for major, minor ions and nutrients. Groundwater samples represent acidic to alkaline nature irrespective of seasons. Larger variations were noted in the chemical constituents with reference to seasonal climate changes. Hill piper plot suggests evolution of groundwater from saline to fresh facies during POM seasons. The ionic ratio plot suggests fresh groundwater discharge, saline intrusion, cation exchange and anthropogenic sources controlling the groundwater chemistry. Nutrients chemistry signifies addition during dryer season due to leaching from artificial fertilizers. On comparison the influence of climate change were identical in surface and groundwater chemistry. Higher concentration recorded during PRM and POM 2015 might be due to higher velocity of water flow due to higher rainfall which has higher dissolved ions and transported more ionic concentrations from the litho units. Changes in precipitation and temperature due to climate change influences seem to control the quality of water in the study area.

Keywords: Submarine groundwater discharge; Nutrient flux; Climate change.

Introduction

Coastal and estuarine ecosystems are prone to human influences due to factors like water salinity, nutrient pollution and other types of consequences. The Intergovernmental Panel on Climate Change (IPCC, 2007) has predicted rise in mean surface temperature of about 2 to 4°C for the next 100 years. Rise in temperature will influence the hydrological cycle in coastal and estuarine regions by increase in precipitation, sea level rise, groundwater pumping, damming of rivers, coastal construction, run off evapotranspiration, land use changes, sea water intrusion, and water quality deterioration and time span of droughts (Wigley and Raper, 1992; Singh and Kumar, 2006). The Submarine Groundwater Discharge (SGD) is isolated as the groundwater flow across the ocean–land interface into the ocean (Church, 1996) which also includes both the fresh groundwater flow from inland aquifers (both confined and unconfined) and sea water circulation into the aquifers due to variations in tidal and seasonal time scales (Michael et al., 2005; Knee and Payton, 2011).

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The main contributors for the SGD are the amount of precipitation received in the drainage area combined with evaporation rate, litho units, hydraulic gradient, hydraulic conductivity and recharge rates in the study area. The SGD is the key pathways for transporting materials like heavy metals, polluted materials, nutrients and fresh groundwater through aquifer from land to coastal ocean (Burnett et al., 2003; Xilong Wang et al., 2014) and is the current topic of research in coastal areas undergoing climate change.

Climate change influences the water environment by changing the quality of water, fresh water bio diversity and alters the ecological characters of the estuary along with marine productivity (Behrenfeld and Kolber, 1999). Thus impaired water quality in the estuaries is of a global problem limiting the utility of water for various purposes including drinking, domestic, food production and other utilities. The quality of water alters during its course of flow through the hydrological cycle aided by the processes as: evaporation, transpiration, uptake by trees and plants, redox reaction, cation exchange, mineral precipitation and dissolution, influences due to fertilizer and pesticide leaching, pollution, and significant biological process (Appelo and Postma, 2005). Understanding the geochemical signatures of the estuarine groundwater quality impart for water resource management (Mondal et al., 2011; Taniguchi, 2002). In the assessment of water quality, hydrochemical data is useful for providing preliminary information on water types, classification of water for various purposes as well as identification of different groundwater aquifers and study of different chemical processes (Saxena et al., 2003; Sarwade et al., 2007).

Numerous workers have attempted for groundwater quality appraisal and subsequent climate change influences in coastal aquifers of the globe (Ramanathan et al., 1993; Windom et al., 2006; Mondal et al., 2011; Srinivasamoorthy et al., 2011; Chidambaram et al., 2013; Zhu et al., 2013; Hwang et al., 2015; Gopinath et al., 2016; Bing Zhang et al., 2017). The coastal groundwater and seawater are the vital mechanisms of the coastal aquifer hydrological system (Sherif and Kacimov, 2007; Kim et al., 2009; Null et al., 2012). The integration and assessment of the coastal hydrological system has been attempted using varied approaches, including (1) estimation and determination using numerical modelling (Zhang et al., 2004; Sarwade et al., 2007; Haider et al., 2015; Gopinath et al., 2016a); (2) geophysical surveys (Oteri,1988; Barrett et al., 2002; Adepelumi et al., 2009; Cordell Johnson et al., 2015); (3) groundwater circulation and mechanism using electrical conductance and water temperature (Beddows et al., 2007; Schmidt et al., 2008; Michael Schubert et al., 2015); (4) submarine groundwater discharge and its subsequent interaction with sea and coastal aquifers (Taniguchi et al., 2006; Chevis, 2015; Lecher et al., 2015); and (5) Ratio plots method for ions like on Cl^-/$HCO_3^-$$Mg^{2+}$/$Ca^{2+}$, EC, and mixing ratios (Kim et al., 2003; Somay and Gemici, 2009; Mondal et al., 2011).

This study investigates the status of surface and groundwater quality in Coleroon river estuary with respect to seasonal and decadal climatic variations. The climate of the study area is generally tropical with hot temperatures (>40°C) all through the year except during the monsoon seasons. Groundwater is the main source of water supply in this region. Due to dense population and increasing industrial and agricultural activities the area is suffering acute groundwater quality problems where, in some distinct locations, the total dissolved solids (TDS) have reached an alarming stage like that of the sea water. Thus, the objective of the present study is to project and characterize the water quality in the estuarine system responses to climate change scenarios.

Study Area

The study was conducted at Coleroon river estuary of Tamilnadu, India that covers 351 sq.km (Figure 1) and lies between Longitude 79°36′50.136″ to 79°50′37.439″ E and Latitude of 11°15′18.363″ to 11°27′18.002″ N. The river Coleroon is a tributary of river Cauvery that originates in Mukkombu located in Trichy district. The total river course is of 160 km and it finally configures Bay of Bengal at Palayar in Nagapattinam district of Tamilnadu. The area's maximum elevation is of 5 m above MSL and it gradually slopes towards the coast. Coleroon river estuary is located in east coast of India with a maximum tide range of 1.2 m which is semi diurnal in nature. The river Coleroon is the main water source for industrial, agricultural and other domestic utilities. Industries like sugar mill, chemical industries, cotton industries and agro industries are sparsely distributed all through the study area. A total of 1000 m^3/d of river and groundwater are being pumped and utilized for the above purposes (MSME, GOI, 2012). The average freshwater discharge in the river is 263 mm/yr (Jain, 2012) with a high surface water runoff (582 mm/yr) during the monsoons and very low and negligible flow (6 mm/yr) during summer seasons (PWD, 2015). The river flow is influenced by back waters during summer due to tidal variations and groundwater extraction scenarios.

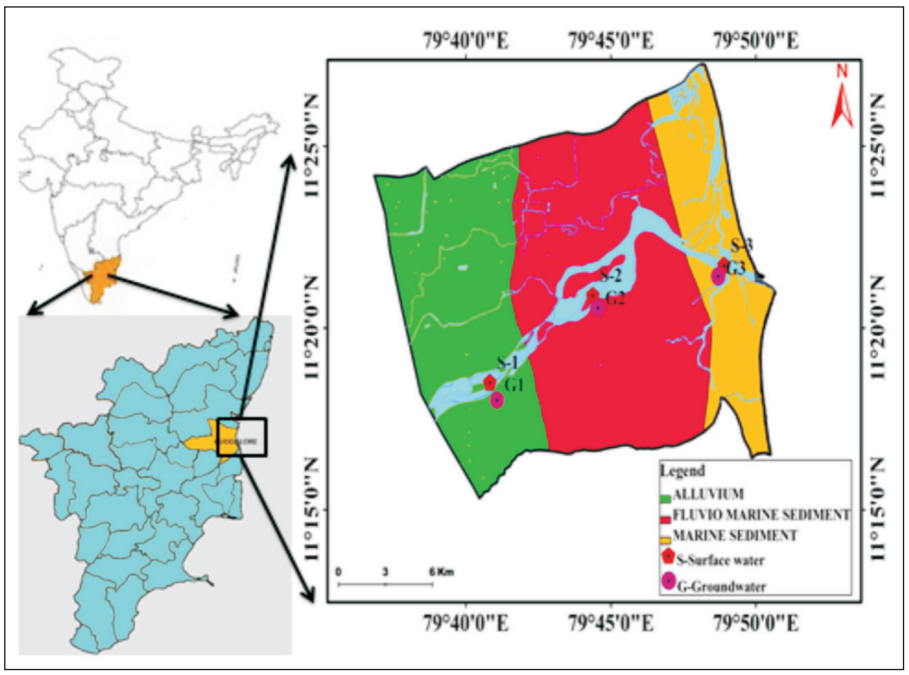

Figure 1: Location and geology of the study area.

Rainfall and Climate

The study area is influenced by hot tropical climate with maximum and minimum temperatures of 37.2°C and 20.6°C during June and December, respectively. Relative humidity in the study area varies from 55% to 87% with highs and lows observed during northeast monsoon and summer seasons. The strength of the wind flow in the study area is moderate with a mean velocity within 6.0 to 14.0 km/h (Srinivasamoorthy et al., 2011). The annual average rainfall of the study area ranges between 762 and 1129 mm of which about 50% of the rainfall is during North-East monsoon (October to January), 33% from June to September during the Southwest monsoon and the rest of the rainfall is during the months of February and March indicating the summer season (Ramesh et al., 2010).

Geology and Hydrogeology

The estuary is predominantly covered by three major geological formations such as alluvium, fluviomarine sediments and beach sands. Beach sands are observed along the coastal tracts of the study area parallel to the shore line with an area of 66.44 sq.km. Fluviomarine sediments are the combination of sandy clay and silt noted along the central parts of the study area with an aerial extent of 170.39 sq.km. Alluvium sands are average in size and noted along the western parts with an area of 112.62 sq.km. The important aquifer of the study area is the unconsolidated shallow aquifer isolated at depth ranging between 3 m and 30 m bgl. Majority of wells (80%) are pumping water from these aquifers for all utilities. Groundwater discharge isolated from the aquifer is of the order of 5.0 to 10.0 litre per second with a drawdown of 0.5 m to 2.0 m (CGWB, 2009). The average freshwater discharge in the river is 263 mm/yr (Jain, 2012) with an annual sediment load of about 24 t/km^2/yr (Vaithiyanathan et al., 1992).

Methodology

Samples were collected from both groundwater and surface water to evaluate the variation in chemical composition and groundwater flux. A total of 12 water samples (three groundwater and three surface water samples/season) were collected during the Pre (June) and Post monsoon (December) season. Water samples were collected at three different locations with reference to variation in distance from coast and lithological features. The groundwater sample G1, was collected from alluvium formation, 20.0 km away from the coast, G2 collected at fluviomarine sediments 9.0 km away from the coast and sample G3 was collected at beach sediments 2.0 km away from the coast. The surface water samples S1, S2 and S3 were collected from Coleroon river within 0.5 km radius of the respective groundwater samples. The samples were collected in acid washed polyethylene 500 ml bottles; prior to the filling all the water samples were filtered immediately

by Whattman filter paper (0.45 μm) and preserved in the refrigerator until they were moved to laboratory for further analysis. The pH, TDS, EC and salinity were measured in situ by Systronics Water Analyzer 371. Methods of collection and analysis of water samples followed are essentially same as given in APHA 1985 and represented in Table 1. The analytical precision for the measurements of cations and anions as represented by Ionic Error Balance (IEB) was computed on the basis of ions expressed in mill equivalents per litre and were found to be within the limit of ±5% (Mandel and Shiftan, 1980; Domenico and Schwartz, 1990).

Table 1: Methods and instruments attempted for chemical analysis

Chemical ions	*Instruments and methods*
EC, pH, TDS and Salinity	Water analyzer with selective electrode and sensor
Na^+, K^+	Flame photometer and ion chromatography
Ca^{2+}, Mg^{2+}	EDTA titro-metric method
Cl^-	Mohr titrimetric method
HCO_3^-	Acidimetric neutralization method
SO_4^{2-}, PO_4^-, H_4SiO_4, F^-	Spectrophotometer
NO_3^-, NH_4^+	UV Visible Spectrophotometer

Result and Discussion

Major elements were determined for six samples in June 2015 and six samples in December 2015. Major hydrochemical parameters are presented in Table 2.

Groundwater Chemistry

The summary of hydrochemical parameters are presented in Table 2. The pH of the groundwater samples ranges from 6.84 to 7.48 and 6.83 to 7.04 during PRM and POM seasons respectively. Groundwater is generally acidic to alkaline in nature irrespective of seasons. Electrical conductivity (EC) ranges between 2602.04 and 17831.02 μS/cm and between 19.77 and 2108.08 μS/cm during PRM and POM, respectively. Total dissolved solids (TDS) indicated widespread variation from 1327.57 to 9097.46 mg/l in PRM, and from 367.23 mg/l to 1075.55 mg/l in POM. Both EC and TDS showed an increasing tendency towards coast during PRM [TDS (G1 – 1327.57 mg/l to G3 – 9097.46 mg/l and EC (G1 – 2602.04 μS/cm to G3 – 17831.02 μS/cm] due to seawater intrusion and/or due to tidal influences (Mondal et al., 2010), lower EC and TDS were observed during POM [TDS (G1 – 367.23/l to G3 – 1075.55 mg/l and EC (G1 – 719.77 μS/cm to G3 – 2108.08 μS/cm] indicating non-saline/freshwater, which might be due to the addition of fresh water by precipitation (Freeze and Cherry, 1979).

The order of dominance of cations and anions during PRM are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > F^- > PO_4^-$, and in POM $Ca^{2+} > Na^+ > K^+ > Mg^{2+} > NH_4^+$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^-$ respectively. Calcium and magnesium during PRM varied from 223.4 to 249.2 mg/l and 14.81 to 129.7 mg/l and in POM it ranges from 49.19 to 160.71 mg/l and 7.5 to 46.58 mg/l respectively. Sodium and potassium concentrations in PRM varied from 130.28 to 2864.71 mg/l and 22 to 45.6 mg/l and in POM it ranges from 22.78 to 94.21 mg/l and 10.5 to 26.23 mg/l respectively. Bicarbonate, chloride, sulfate, nitrate, phosphate and fluoride in PRM ranges between 155.00 to 244.65 mg/l, 385.23 to 5441.1 mg/l, 14.5 to 50.9 mg/l, 1.35 to 1.42 mg/l, 0.35 to 1.00 mg/l and from 1.2 to 1.5 mg/l respectively. During POM concentrations varied from 285.4 to 468.00 mg/l, 76.35 to 462.18 mg/l, 1.2 to 10.7 mg/l, 1.59 to 1.67 mg/l, 0.1 to 0.45 mg/l and from 0.4 to1.1 mg/l respectively. Ammonium and dissolved silica concentrations during PRM range from 1.3 to 2.3 mg/l and 25 to 67 mg/l and during POM it varied from 1.08 to 1.12 mg/l and 27 to 35 mg/l respectively. During POM calcium and bicarbonate ions are dominating indicating both ground and surface water to be fresh in nature but during PRM, sodium and chloride seems to be dominating indicating the saline nature of water resources.

During both the seasons the release of calcium might be due to dissolution of precipitates of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) during recharge along the upstream (Gopinath et al., 2015). The sodium might have been due to weathering of feldspar minerals during POM and might be due to addition of sea water and/or tidal influences during PRM season (Chidambaram et al., 2010). Potassium might have been due to application of fertilizers and K-feldspar weathering from the upstream (Howari and Banat, 2002). Bicarbonate is an effective tool to isolate fresh water. Bicarbonates were found to be higher during POM (G1 – 468 mg/l) might be due to the action of CO_2 upon basic material of soil and rock weathering from fresh water. Lower in PRM (G1 – 155.9 mg/l) might be due to ions exchange processes (Srinivasamoorthy et al. 2011). Sulfates in aquatic environment are mainly due to breaking down of organic substances from weathering soil or water.

Table 2: Concentration of major ions from groundwater and surface water samples from the study area

Well. No	*pH*	*TDS*	*EC*	*Salinity*	*Na^+*	*K^+*	*Ca^{2+}*	*Mg^{2+}*	*HCO_3^-*	*Cl^-*	*SO_4^{2-}*	*NO_3^-*	*PO_4^-*	*H_4SiO_4*	*NH_4^+*	*F^-*
PRM																
G1	6.84	1327.57	2602.04	1580.44	130.28	22.00	248.20	14.81	155.90	385.23	14.50	1.40	0.35	40.00	1.30	1.50
G2	7.06	2587.90	5072.28	3080.83	541.25	28.13	223.40	56.21	182.60	1275.24	43.50	1.42	0.85	67.00	1.60	1.30
G3	7.48	9097.46	17831.02	10830.31	2864.71	45.60	249.20	129.70	244.65	5441.10	50.90	1.35	1.00	25.00	2.30	1.20
S1	6.92	1070.72	2098.61	1274.67	106.80	27.64	185.20	20.13	362.50	294.30	23.00	2.85	0.65	44.75	1.70	1.20
S2	7.27	4890.68	9585.72	5822.23	1341.57	36.90	251.60	173.84	238.10	2762.35	29.54	2.40	1.02	50.40	1.84	1.12
S3	7.62	22931.73	44946.20	27299.68	7981.08	163.17	295.50	364.64	187.34	13829.52	56.80	2.67	1.30	46.30	2.05	1.36
POM																
G1	6.83	367.23	719.77	437.18	22.78	12.97	49.19	9.62	468.00	76.35	1.20	1.59	0.45	35.00	1.08	1.10
G2	6.92	481.95	944.62	573.75	41.68	10.50	76.85	7.50	348.00	123.50	3.30	1.64	0.28	32.00	1.10	1.00
G3	7.04	1075.55	2108.08	1280.42	94.21	26.23	160.71	46.58	285.40	462.18	10.70	1.67	0.10	27.00	1.12	0.40
S1	6.76	514.55	1008.51	612.55	46.70	10.58	84.12	9.46	210.80	104.53	14.30	0.59	0.15	32.50	0.22	0.60
S2	6.72	555.98	1089.71	661.88	47.30	12.93	91.80	12.07	213.50	133.86	11.70	0.50	0.12	31.41	0.24	0.55
S3	6.90	1265.97	2481.30	1507.11	224.50	32.19	88.63	59.44	234.70	563.05	23.10	0.56	0.65	38.00	0.25	0.90

PRM – Pre Monsoon , POM – Post Monsoon, G – Groundwater, S – Surface water. All ions with TDS and salinity in mg/l, EC (electrical conductivity) in Micro S/cm, pH in standard units.

Sulfates was found to be higher in PRM (50.60 mg/l) due to saline water influences and was observed lower during POM (10.70 mg/l) which might be due to recent recharged water during precipitation (Chapelle and Mcmahon,1991). Chloride is found to be higher (G3 – 5441.10 mg/l) during PRM, indicating the impact of saline water, anthropogenic sources and ions exchange process activated in the study area (Srinivasamoorthy et al., 2012) and lower chlorides observed during POM (G3 – 462.18 mg/l) might be due to fresh water discharge (Mondal et al., 2011a). In general groundwater chemistry seems to be influenced by saline water intrusion/tidal influences during PRM, due to lower flow of SGD due to absence of precipitation and during POM the water quality significantly increases signifying the impact of precipitation and subsequent recharge of shallow aquifer which tend to increase the SGD (Bing Zhang et al., 2017).

Surface Water Chemistry

The pH of the surface water samples ranged from 6.92 to 7.62 and 6.72 to 6.9 during PRM and POM, respectively (Table 2). Surface water is generally acidic to alkaline in nature irrespective of seasons. Electrical conductivity (EC) ranges between 2098.61 and 44946.2 µS/cm and between 1008.51 and 2481.3 µS/cm during PRM and POM, respectively. Total dissolved solids (TDS) indicated widespread variation from 1070.2 to 22931.7 mg/l in PRM, and from 514.55 mg/l to 1265.97 mg/l in POM. Both EC (G1 – 2602.04 µS/cm to G3 – 17831.02 µS/cm) and TDS (G1 – 1327.57 mg/l to G3 – 9097.46 mg/l) showed increasing tendency towards coast during PRM might be due to the tidal influences and lower EC (G1 – 719.77 µS/cm to G3 – 2108.08 µS/cm) and TDS (G1 – 367.23 mg/l to G3 – 1075.55 mg/l) during POM might be due to addition of fresh water by monsoonal influences (Rodgers et al., 2004). The order of dominance of cations and anions during PRM are $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > F^- > PO_4^-$, and in POM $Ca^{2+} > Na^+ > K^+ > Mg^{2+} > NH_4^+$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^- > PO_4^-$ respectively.

Sodium and potassium concentrations during PRM varied from 106.8 to 7981.08 mg/l and 27.64 to 163.17 mg/l and during POM it varied from 46.7 to 224.5 mg/l and 10.58 to 32.19 mg/l respectively. Calcium and magnesium during PRM ranged from 185.52 to 295.5 mg/l and 20.13 to 364.64 mg/l and during POM, it ranges between 84.12 to 91.8 mg/l and 9.46 to 59.44 mg/l respectively. Bicarbonate, chloride, sulfate, nitrate, phosphate and fluoride during PRM ranged from 187.34 to 362.5 mg/l, from 294.3 to 13829.5 mg/l, from 23.00 to 56.8 mg/l, from 2.4 to 2.85 mg/l, from 0.65 to1.3 mg/l and from 1.12 to 1.36 mg/l while during POM it varied from 210.8 to 234.7 mg/l, from 104.53 to 563.05 mg/l, from 11.7 to 23.1 mg/l, from 0.5 to 0.59 mg/l, from 0.12 to 0.65 mg/l and from 0.55 to 0.9 mg/l respectively. Ammonium and dissolved silica concentrations in PRM ranged from 1.7 to 2.05 mg/l and 44.75 to 50.4 mg/l and during POM from 0.22 to 0.25 mg/l and 31.41 to 38 mg/l respectively.

All the ionic concentrations were higher during PRM due to ions exchange, mixing and tidal influence from Bay of Bengal and lower in POM might be due to adding of fresh water from the catchment regions. The sources for Ca^{2+} might be due to the weathering of feldspars, pyroxene and amphiboles from the litho units of the study area (Gopinath et al., 2016). Higher Na^+ might be due to the dissolution of halite minerals and seawater influenced by tide (Chidambaram et al., 2013). Potassium was found to be higher in PRM (G1 – 22 mg/l) during PRM season might be due to the application of fertilizers and weathering of K-feldspars and lower concentration (10.58 mg/l) during POM might be due to mixing of fresh water by rain (Zhang et al., 2017). Sulfate was found to be higher in PRM (56.80 mg/l) because of tidal effects and lower in POM (23.10 mg/l) due to monsoon effect (Srinivasamoorthy et al., 2011). Cl^- is found to be higher (G3 – 13829.52 mg/l) indicating the impact of saline water, anthropogenic sources and ions exchange process in PRM (Wang et al., 2015) and lower (G3 – 563.05 mg/l) was observed during POM season might be due to fresh water discharge (Mondal et al., 2011). In general, surface water chemistry found to be influenced by coastal processes in PRM and addition of fresh water sources during POM might have played a significant role in controlling the dissolved ions (Taniguchi et al., 2007).

Piper Trilinear Diagram

Hydrochemical concepts support mechanisms of mineralization and salinization in groundwater systems, and an archive of paleoenvironmental information (Pierre et al., 2005). The classification of hydrochemical facies as proposed by Piper (1944) for both groundwater and surface water is depicted in Figure 2. The plot shows water types spreading within CaMg-HCO_3, NaK-NO_3Cl, NaK-HCO_3, CaMg-NO_3Cl, Ca-Cl, Na-HCO_3, Ca-HCO_3 and Na-Cl types irrespective of seasons. Groundwater samples tend from fresh water facies (G1 – CaNa-ClHCO_3) to mixed water facies (G2 – NaCa-Cl) and finally to saline water facies (G3 – Na-Cl) during

PRM but during POM, it is fresh (G1 – CaNa-HCO_3Cl facies, G2 – CaNa-ClHCO_3 facies to mixed facies G3 – CaNa-ClHCO_3) in nature. Surface water samples depict freshwater facies (S1 – CaNa-ClHCO_3 facies) to saline water (S2 and S3 – Na-Cl facies) during PRM season, and during POM, the samples shifts from saline facies to mixed facies (S1 – CaNa-HCO_3Cl facies, S2 and S3 – CaNa-ClHCO_3) indicating the influence of monsoonal rainfall which also significantly increases the SGD.

Groundwater samples seem to be intruded by saline water in G3 (Na-Cl facies) and mixing was observed in G2 and G1 samples during PRM which might be due to absence of precipitation and might also be due to higher drafting of groundwater. During POM the same samples exhibited fresh facies which might be due to the dilution chemistry and seem to influence precipitation which also triggers SGD (Halim et al., 2010). Surface water chemistry seems to be influenced by tidal influences during PRM where the water chemistry shifts from fresh (CaNa-ClHCO_3) facies along the upstream directions to saline water (Na-Cl facies) at the configuring point which might be due to lower surface flow due to lack of precipitation. During POM season the water facies oscillated within the fresh water and mixed water facies indicating the influence of precipitation and SGD.

Ionic Ratios

Ionic ratio plots confer individual ionic contribution responsible for the change in hydrochemical nature of groundwater. Hence it is inevitable to use the ionic ratio plots to study the characteristic ion ratios as potential sources. By plotting the ionic concentrations, the groundwater chemical characteristics can be easily understood along with determination of sources and process responsible for the enrichment of those ions (Ahmed, 2013).

Mg^{2+}/Ca^{2+} and Cl^-/HCO_3^- Ratios

The possibility of seawater contamination was examined using the Mg^{2+}/Ca^{2+} and Cl^-/HCO_3^- ratios (all values are in epm), as suggested by Hem (1989). The Mg^{2+}/Ca^{2+} ratio (Figure 3) is used as an indicator for delineating seawater–freshwater interactions and interface. Mondal et al. (2011) observed that higher Mg^{2+}/Ca^{2+}molar ratios (1.00) indicated the transformation of fresh groundwater to saline water in coastal aquifers. The Mg^{2+}/Ca^{2+} ratios of groundwater at wells G1 (PRM – 0.099 and POM – 0.324) and G2 (PRM – 0.418 and POM – 0.162) did not exceed 1 in both seasons but in location G3 (PRM – 0.864 and POM – 0.481) it approaches 1 during PRM with a subsequent decrease during POM season. From ratio plot G1 and G2 locations Ca^{2+} was higher than Mg^{2+}; this might be due to the release of Ca^{2+} from weathering from the litho units of the study area. In G3, the concentration of Mg^{2+} and Ca^{2+} were nearly equal, might be due to the addition of Mg^{2+} from seawater due to excess drafting of groundwater (Mondal et al., 2008). During PRM, G1 shows fresh nature and G2 shows mixed nature and G3 were observed to be saline in nature. During POM, irrespective of locations all the samples exhibited fresh water due to the possible sources of natural recharge. Surface water samples show fresh in S1 (PRM – 0.180 and POM – 0.186) and saline (PRM – 1.148) to fresh (POM – 0.218) in S2 and saline in S3 (PRM – 2.050 and POM – 1.114) irrespective of seasons. Fresh water ($Mg^{2+}/Ca^{2+}< 1$) is mainly due to the addition of atmospheric recharge and saline water ($Mg^{2+}/Ca^{2+}>1$) to be influenced by tidal processes (Gurumoorthy et al., 2004).

The Cl^-/HCO_3^- ratios of groundwater samples were observed to be G1 (PRM – 1.416 and POM – 0.842) and G2 (PRM – 6.305 and POM – 1.163) and G3 (PRM – 32.80 and POM – 3.250) respectively. The ratio decreases during POM when compared with PRM, might be due to SGD and fresh water recharge (Srinivasamoorthy et al., 2011). The surface water samples express S1 (PRM – 1.397 and POM – 0.853) and S2 (PRM – 19.964 and POM – 1.078) and S3 (PRM –127.033 and POM – 4.128) respectively. The ratio increases in PRM when compared with POM due to saline water approaches by tide and insignificant amount of fresh water flow (Saravanan et al., 2016).

$(Ca^{2+}+Mg^{2+})/(K^++Na^+)$ vs log Cl^-

The correlation of specific ions are utilized to isolate the prominent geochemical process activated in the study area. Groundwater samples influenced by sea water might contain greater Na^+, K^+ and Cl^- ions along with which there might be also an increase in Ca^{2+}ions due to cation exchange reaction (Chidambaram et al., 2010). From Figure 3 it is identical that an increase of $(Ca^{2+}+Mg^{2+})/(K^++Na^+)$ ratio (in meq/l) is also influenced by an increase in Cl^- ions. This is mainly due to the process of cation exchange between the Ca^{2+} and Mg^{2+}ions which gets absorbed by the mineral phases in the aquifer matrix and addition of Na^+ in the groundwater environment, might be due to sea water intrusion (Gao et al., 2007). From the plot majority of groundwater samples (Figure 4) during POM fall in fresh water domain indicating the flow of fresh water from SGD. The variations in chemical constituents are mainly due to weathering, recharge and cation exchange

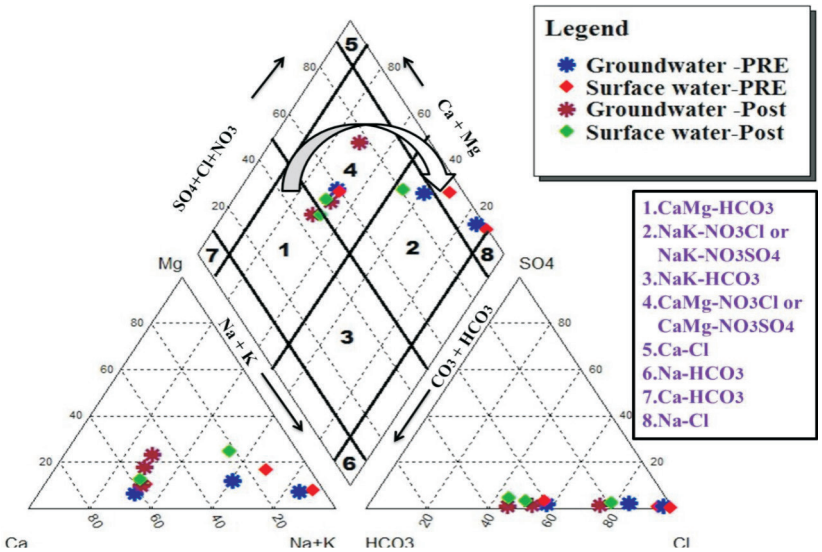

Figure 2: Hill piper plot for the water samples.

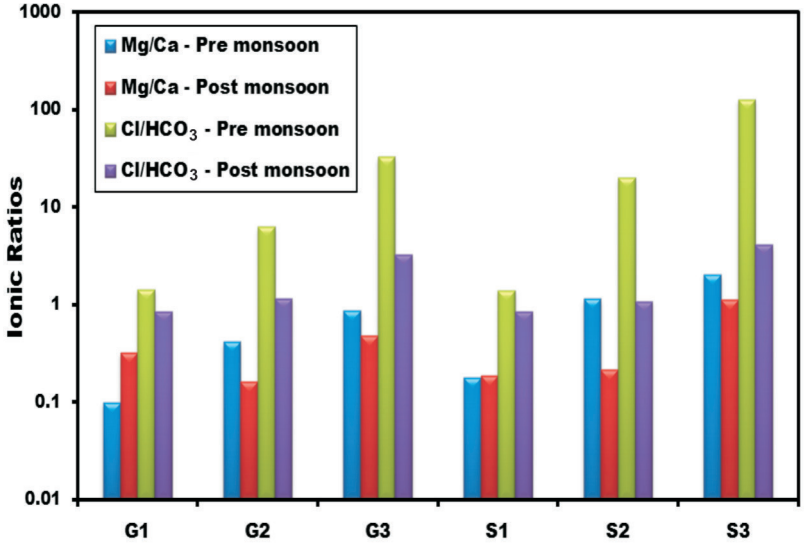

Figure 3: Mg^{2+}/Ca^{2+} and Cl^{-}/HCO_3^{-} ratios for water samples.

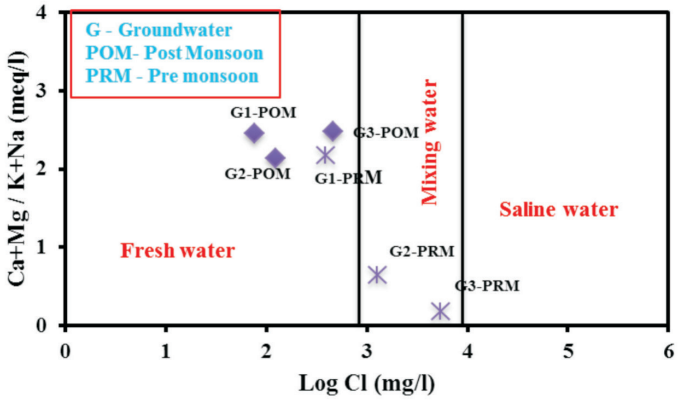

Figure 4: $(Ca^{2+}+Mg^{2+})/(K^{+}+Na^{+})$ vs log Cl^{-} for groundwater samples.

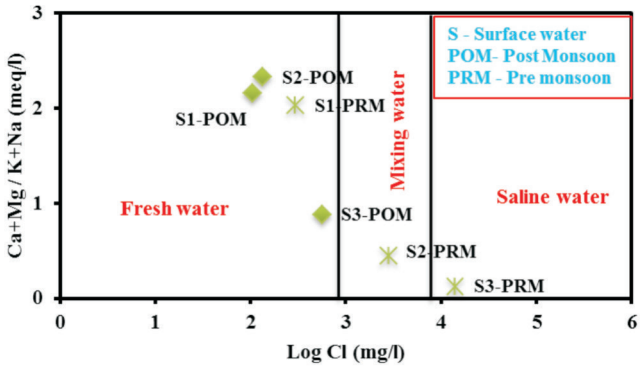

Figure 5: $(Ca^{2+}+Mg^{2+})/(K^{+}+Na^{+})$ vs log Cl^{-} for surface water samples.

processes (Gao et al., 2007). During PRM, sample G1 represents freshwater flow as SGD fluxes and sample G2 exhibited the seawater fresh water mixing zone (subterranean estuary). The sample G3 which was located very near to the coast exhibit saline water due to intrusion of sea water from Bay of Bengal. In general, during POM season, surface flow (Figure 5) rate at the Coleroon river is very high and fresh in nature, due to monsoon recharge and during PRM it changes from fresh to saline nature due to lower flow observed due to absence of precipitation and tidal intrusion activities.

Nutrients Concentration

Nutrients are the primal sources for estimating the SGD sources that are derived mainly due to the applications of fertilizers in agricultural fields (Rodellas et al., 2014). To enhance the rate of harvest, farmers apply fertilizers like urea, ammonium sulphate, ammonium nitrate, ammonium chloride, di-ammonium phosphate (DAP) and N:P:K and pesticides (Ramanathan et al., 1999). The applied fertilizers tend to dissolve with water by leaching until it reaches the aquifers (Senal et al., 2011). Due to continuous discharge of nutrients in coastal regions, it tends to increase the microorganism and creates algal blooms (Lee et al., 2010) which also influences the ecological and environmental significance of the coastal regions. The nitrogen and phosphorus limiting phytoplankton growth and changing coastal climate by increasing marine productivity (Windom et al., 2006). The nutrients tend to increase from land to the coast due to hydraulic gradient and SGD (Slomp et al., 2004).

The concentration of nitrate, phosphate and ammonium seems to vary irrespective of seasons (Figures 6 and 7). Higher nutrients (G1 – 22.59, G2 – 22.92 and G3 – 21.79 μmol L^{-1}) were observed during PRM when compared with POM (G1 – 9.52, G2 – 8.87 and G3 – 9.03 μmol L^{-1}). The concentration of nitrate, phosphate and ammonia are documented in Table 3. In G1 the concentration of NO_3^-, PO_4^- and NH_4^+ were 22.59, 3.69 and 72.07 μmol L^{-1}1 respectively during PRM and 9.52, 1.58, and 12.02 μmol L^{-1} respectively during POM. In G2 the concentrations range 22.92, 8.95 and 88.70 μmol L^{-1} during PRM and 8.87, 1.26 and 13.31 μmol L^{-1} in POM respectively. In G3 the nutrients NO_3^-, PO_4^- and NH_4^+ were 21.79, 10.53 and 127.51 μmol L^{-1} respectively during PRM and 9.03, 6.84 and 13.86 μmol L^{-1} respectively during POM season. In general, nutrients were found to be higher during PRM when compared with POM, which might be due to excess application of fertilizers and absence of water for subsequent dilution (Sugita and Nakane, 2007). In surface water samples nutrients like NO_3^-, PO_4^- and NH_4^+ ranges between 45.99, 6.84 and 94.25 μmol L^{-1} in PRM and 25.65, 4.74 and 59.88 μmol L^{-1} in POM season respectively in Sample S1. In S2 the concentration varies as 38.73, 10.69 and 102.01 μmol L^{-1} in PRM and 26.45, 2.95 and 60.98 μmol L^{-1} in POM season respectively. In S3 the concentration ranges as 43.09, 13.69 and 113.65 μmol L^{-1} in PRM and 26.94, 1.53 and 62.09 μmol L^{-1} in POM season respectively. Surface water nutrients were found to be lower in POM than PRM, which might be due to the influence of precipitation linking high surface flow in the Coleroon River.

Decadal Climate Change Influences on Temperature, Precipitation, Surface Water and Groundwater Quality

The impact of decadal climate change on groundwater quality is unique since it influences the hydrogeological process and groundwater resources (Dettinger and Earman, 2007). The emission of enhanced greenhouse gases into the atmosphere will add to global warming and also increase the temperature and precipitation due to increase in water holding capacity of atmosphere (Green et al., 2011). Higher temperature increases

Table 3: Nutrients concentration from the study area

Locations	*NO_3-PRM*	*NO_3-POM*	*PO_4-PRM*	*PO_4-POM*	*NH_4-PRM*	*NH_4-POM*
G1	22.59	9.52	3.69	1.58	72.07	12.20
G2	22.92	8.87	8.95	1.26	88.70	13.31
G3	21.79	9.03	10.53	6.84	127.51	13.86
S1	45.99	25.65	6.84	4.74	94.25	59.88
S2	38.73	26.45	10.69	2.95	102.01	60.98
S3	43.09	26.94	13.69	1.53	113.65	62.09

PRM – Pre Monsoon, POM – Post Monsoon, G – Groundwater, S – Surface water, Nutrients Expressed in Micro mole per Liter.

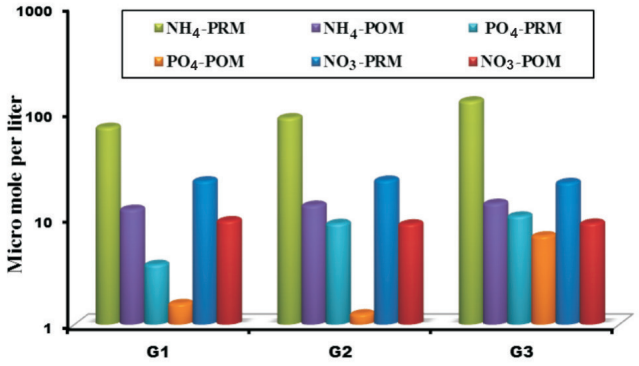

Figure 6: Nutrients concentration for groundwater samples.

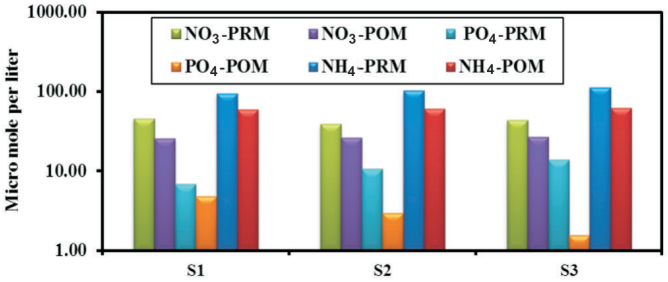

Figure 7: Nutrients concentration for surface water samples.

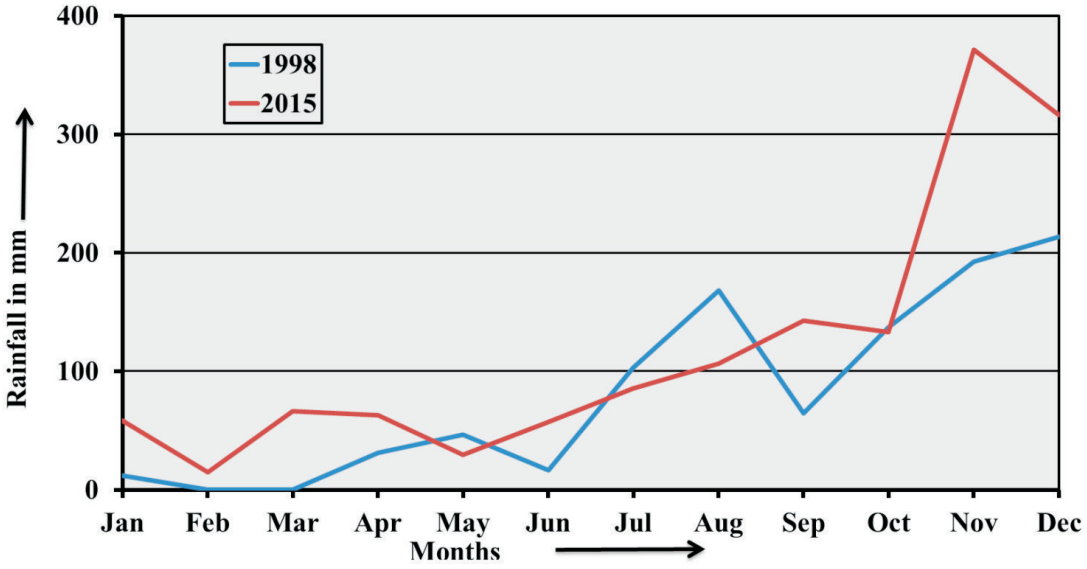

Figure 8: Month-wise decadal variation of rainfall.

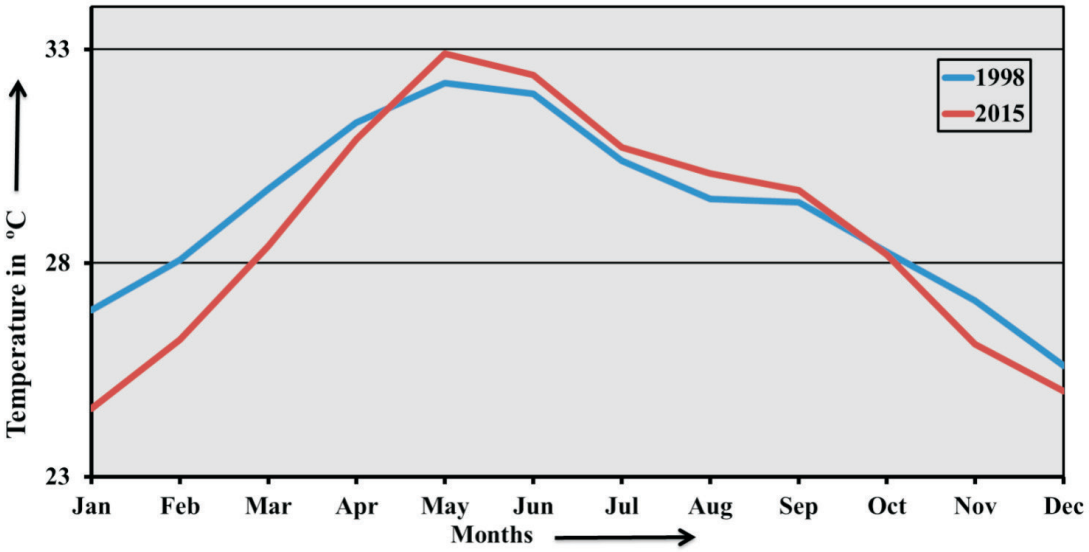

Figure 9: Month-wise decadal variation of temperature.

evapotranspiration resulting in reduced runoff and decline in groundwater levels and in contrast higher precipitation than average and lower temperature will increase recharge and tends to decrease water demand (Rosenberg et al., 1999). In semi arid regions like that of the present study, small change in precipitation will tend to alter the recharge values (Woldeamlak et al., 2007) and influence the subsurface hydrologic processes that control the infiltration rate. Due to the strong correlation of precipitation and temperature variability with water quality and quantity (Castro et al., 2007; Kundzewicz et al., 2007) attempt has been made to compare and correlate the variations of temperature, precipitation, major ion and nutrient chemistry for the years 1998 and 2015 respectively. During the year 1998, the minimum and maximum recorded temperatures were during May (32.21°C) and December (25.60°C) respectively (Table 4) with an average of 29.20°C. During 2015 (Figure 8), the minimum and maximum recoded temperatures were during May (32.90°C) and December (25.00°C) respectively with an average of 28.76°C. When compared with 2015 the year 1998 recorded with maximum average temperature.

Table 4: Rainfall and temperature data for 1998 and 2015

Month/years	*Temperature in °C*		*Rainfall in mm*	
	1998	*2015*	*1998*	*2015*
January	26.89	24.60	12.04	58.30
February	28.07	26.20	0.27	15.00
March	29.74	28.40	0.10	66.50
April	31.29	30.90	31.25	62.80
May	32.21	32.90	46.48	29.80
June	31.96	32.40	16.48	57.30
July	30.39	30.70	102.86	85.60
August	29.49	30.10	168.24	106.40
September	29.42	29.70	64.80	142.80
October	28.26	28.20	136.85	133.00
November	27.12	26.10	192.42	371.10
December	25.60	25.00	213.30	316.50

For precipitation (Figure 9), maximum was observed during December (213.30 mm) and minimum during March (0.10 mm) with an average of 82.09 mm for the year 1998. During 2015, maximum precipitation has been observed during December (371.10 mm) and minimum during February (15.00 mm) with an average of 120.42 mm. Higher precipitation were noted during 2015 when compared to 1998, which might be due to El Nino weather pattern prevailing in Asia and Pacific during 2015-2016 which is said to be the strongest since 1998 (WMO, 2015). Since aquatic systems strongly correlate with local changes in precipitation which has direct impact in altering the inflows to the river, runoff and infiltration capacity of the groundwater systems along with chemical constituents to the river and groundwater systems (IPCC, 2008, Kundzewicz et al., 2009) especially in the semi arid regions. Attempt has also been made to correlate the EC and TDS concentrations of both surface (Ramanathan et al., 1999) and groundwater samples (CGWB, 1998) during 1998 and 2015 for two different seasons (Pre monsoon and Post monsoon) respectively. On comparison (Figure 5), surface water chemistry (Figure 10) during PRM 1998 were significantly higher, TDS (11992 mgL^{-1}) and EC (27333 µS/cm) when compared with TDS (9631.0 mgL^{-1}) and EC (18876.8 µS/cm) during PRM 2015 and the same trend was also noted during POM, 1998 with TDS (13218 mgL^{-1}) and EC (18467 µS/cm) when compared with TDS (778.00 mgL^{-1}) and EC (1526.5 µS/cm) during POM 2015 indicating the influence of changing weather patterns (Table 5).

Table 5: Surface water chemistry for 1998 and 2015

Chemical ions	*PRM-1998*	*PRM-2015*	*POM-1998*	*POM-2015*
pH	8.1	7.3	8.0	6.8
EC	27333.0	18876.8	18467.0	1526.5
TDS	11992.0	9631.0	13218.0	778.8
Na^+	2401.0	3143.2	3071.0	106.2
K^+	158.0	75.9	140.0	18.6
Ca^{2+}	190.0	244.1	322.0	88.2
Mg^{2+}	382.0	186.2	675.0	27.0
Cl^-	7296.0	5628.7	6267.0	267.1
HCO_3^-	194.0	262.6	195.0	219.7
SO_4^{2-}	1346.0	36.4	2533.0	16.4
PO_4^-	0.2	1.0	0.2	0.3
F^-	0.2	1.2	0.3	0.7
H_4SiO_4	22.0	47.2	13.2	34.0

PRM – Pre Monsoon, POM – Post Monsoon. All ions with TDS in mg/l, EC (electrical conductivity) in Micro S/cm, pH in standard units.

Lower precipitation and higher temperature might be the reason for increased chemical constituents enrichment in the surface water chemistry during 1998. On the other hand decreasing temperature and increased precipitation aided with El Nino weather pattern is well felt in the decreased concentration of EC and TDS values during 2015. But a different trend is observed in groundwater chemistry (Figure 11) during PRM 1998 (Table 6), the concentration

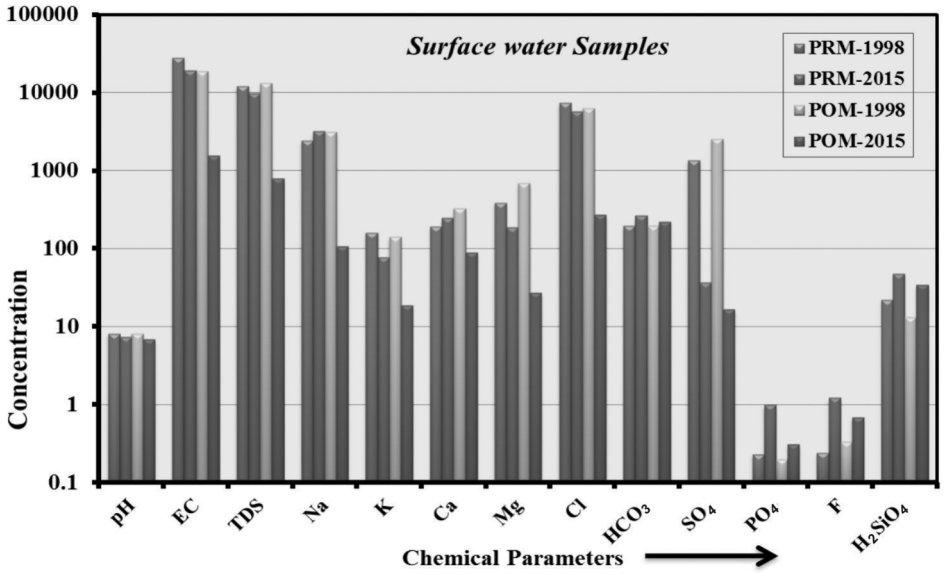

Figure 10: Surface water chemistry variation 1998 and 2015.

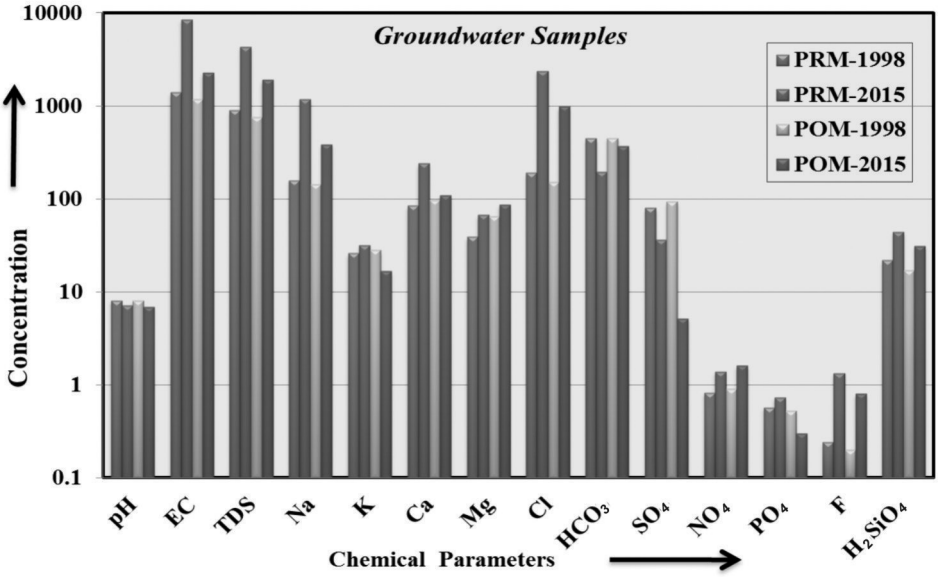

Figure 11: Groundwater chemistry variation 1998 and 2015.

of TDS (889.6 mgL^{-1}) and EC (1390.3 µS/cm) were lower when compared with PRM 2015, TDS (4337.6 mgL^{-1}) and EC (8501.8 µS/cm) respectively. The same trend followed during the POM 1998 and 2015 for EC (1185.3 µS/cm) and (2258.7 µS/cm) and TDS (758.6 mgL^{-1}) and (1899.7 mgL^{-1}) respectively. Higher concentration recorded during PRM and POM 2015 might be due to higher velocity of water flow due to higher rainfall which might have dissolved and transported more ionic concentrations from the litho units in contact (Ngabirano et al., 2016) due to the presence of highly permeable soils in the study area (Gopinath et al., 2015). Changes in precipitation and temperature due to climate change influences seem to control the quality of water in the study area. The TDS and EC concentrations of surface water showed a decreasing tendency with reference to shift in rainfall and temperature and the opposite has been noted in groundwater samples indicating the increased concentration which is linked with subsequent flushing and dissolution due to higher vertical hydraulic gradient and higher vertical groundwater flow.

Table 6: Groundwater water chemistry for 1998 and 2015

Chemical ions	*PRM-1998*	*PRM-2015*	*POM-1998*	*POM-2015*
pH	8.1	7.1	8.0	6.9
EC	1390.0	8501.8	1185.3	2258.7
TDS	889.6	4337.6	758.6	1899.7
Na^+	158.0	1178.8	142.0	387.0
K^+	26.0	31.9	28.0	16.6
Ca^{2+}	84.0	240.3	97.0	110.0
Mg^{2+}	39.0	66.9	65.0	86.0
Cl^-	191.0	2367.2	152.0	980.54
HCO_3^-	445.0	194.4	451.2	367.1
SO_4^{2-}	80.0	36.3	93.0	5.1
NO_3^-	0.8	1.4	0.9	1.6
PO_4^-	0.6	0.7	0.5	0.3
F^-	0.2	1.3	0.2	0.8
H_4SiO_4	21.8	44.0	17.0	31.3

PRM – Pre Monsoon , POM – Post Monsoon. All ions with TDS in mg/l, EC (electrical conductivity) in Micro S/cm, pH in standard units.

Conclusion

The study summarizes the variations in chemical constituents and nutrient fluxes along with SGD with reference to seasonal climate changes and decadal variations. Both ground and surface water samples were found to be influenced strongly by seasonal and temporal variations. Higher concentrations observed during PRM suggests absence of SGD due to subsequent precipitation and lower concentrations observed during POM depicts greater flow with subsequent dilution of chemical constituents. Piper plot suggests hydrochemical facies altering from saline to fresh groundwater during POM season. Both Na^+ and Cl^- ions found to be decreasing in groundwater samples towards coast during POM season. Representative ionic ratios, Mg^{2+}/Ca^{2+}, HCO_3^-/Cl^-, and $Ca^{2+}+Mg^{2+}/K^+ + Na^+$ vs log Cl^- levels differentiated groundwater strongly undergone recharge by monsoonal climate. Nutrients followed the same trend like the major ions suggesting excess discharge of fresh groundwater as SGD during monsoon period. Comparison of temperature and precipitation between 1998 and 2015 signifies higher temperature and lower precipitation during 1998 and lower temperature and higher precipitation during 2015 correlated with El Nino influences. Comparison between TDS and EC between 1998 and 2015 shows decreasing trend with reference to rainfall and temperature and the reverse has been observed in groundwater samples which showed higher concentration due to subsequent flushing and dissolution along the vertical groundwater flow. Both seasonal and decadal variations seem to influence the quality of water in the study area.

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