

Role of hydrogeochemical process in increasing groundwater salinity in the central Godavari delta

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ABSTRACT

Groundwater salinization is an ever increasing problem in coastal aquifers due to seawater intrusion resulting from excessive groundwater withdrawals, lithological conditions of the aquifer and industrial and agriculture pollutant loads. Identification of salinity sources is challenging and a prerequisite for the protection of coastal fresh water aquifers. The present aim of the study is to identify the salinity sources and to understand its dynamics in the central Godavari delta, Andhra Pradesh where groundwater is highly saline with total dissolved solids (TDS) of ~5000 mg/L at shallow depths of <3 m bgl. Groundwater samples were collected from 42 representative observation wells in the area and analyzed for major ions and stable isotopes ($\delta^{18}\text{O}$). Different hydro-chemical mixing models and multivariate statistical techniques, including factor and cluster analysis, are applied to these data sets. The results revealed that very high salinity (~25,000 mg/L) in pumping wells is due to up-coning of salt water and the salinity is palaeo in origin. The salinity in the wells along the drains and near the coast (~10,000 mg/L) is due to the infiltration of marine waters resulting from backwaters and intrusion of seawater along the drains. The salinity (~5000 mg/L) in the wells away from the coast is attributed to dissolution of evaporites in the groundwater and ion exchange process.

Key words | central Godavari delta, ion exchange, salinity, salt water intrusion, stable isotopes

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INTRODUCTION

In recent years, an increase in the salinity of groundwater has become a major problem in coastal aquifers, and this makes the use of groundwater unfit for various purposes (Surinaidu *et al.* 2013; Shapouri *et al.* 2016). On the other hand seawater intrusion into the inland aquifers is a major threat due to heavy groundwater exploration to meet the rising demands for different sectors (Todd 1982; Raghunath 2005). Groundwater and sea water are an integral part of hydrological systems in coastal areas and the balance between these fluids is very sensitive and can easily be disturbed (Mondal *et al.* 2010). The driving factors that influence seawater intrusion or the fresh groundwater and seawater interactions are viz., topography, sub-surface hydraulic properties, temporal variation in precipitation, temporal migration of seawater into shallow unconfined

aquifers, tidal and estuarine activity, sea-level rise, and excessive groundwater withdrawals (Cruz & Silva 1999; Kim *et al.* 2009; Mondal *et al.* 2010). Groundwater salinization in the coastal aquifers is influenced by many factors, such as the lithology of the aquifer, the quality of recharge water, and the type of interaction between the liquid and mineral phases (Helena *et al.* 2000; Somay & Gemici 2009). In general, high salinity in the coastal aquifers could occur from several sources other than seawater intrusion that include pollution from various origins, such as industrial and agriculture wastes, and also from brines which are not directly connected to the present sea (Surinaidu *et al.* 2013, 2014).

In such cases, classification of wells according to their water quality and their source can be very difficult.

Characterization, interpretation and understanding of groundwater chemistry are essential for not only identifying the source of the contamination, but also to understand and characterize the factors controlling the basic hydrochemistry. The classification and source identification could provide useful information for policy makers of the groundwater resource management. Composite diagrams (Back 1966; Hendry & Schwartz 1990; Howard & Mullings 1996; Marie & Vengosh 2001) and saturation indices (Nordstrom *et al.* 1989; Jeong 2001) are useful tools to understand the interaction between groundwater and the host rock/aquifer. On the other hand stable isotopes could be a better tool for characterizing groundwater flow, identifying potential sources of groundwater contamination and salinity source (Clark & Fritz 1997; McCarthy *et al.* 1998; Mancini *et al.* 2002; Hunkeler *et al.* 2004; Morrill *et al.* 2006; Vinson *et al.* 2011; Ya & Jiu 2012). Multivariate statistical techniques are very effective and are the best way to classify and distinguish very complex hydrochemical changes that control the hydrochemical dynamics in coastal aquifers. Many researchers have successfully applied multivariate methods to interpret various hydrochemical processes (Ritzi *et al.* 1993; Helena *et al.* 2000).

The present study focused on the understating of the dynamic hydrochemical process occurring in the central Godavari coastal alluvial aquifer using different hydrochemical composite models, stable isotopes and multivariate statistical methods that comprise of factor and cluster analysis. The data is based on chemical, physical parameters and isotopic signatures that are collected in the pre-monsoon (June) and post-monsoon (October) periods of 2006 and 2007.

GEOLOGIC AND HYDROLOGIC SETTINGS OF THE STUDY AREA

The central Godavari deltaic region is situated in the East Godavari District of Andhra Pradesh, India, bounded by the Bay of Bengal in the eastern side and Vainateya River to the west, and plain lands of an alluvial nature to the north (Figure 1). The area is occupied by quaternary alluvial derived from the Godavari River and has a very gentle land slope of about 0.001 (Rao 1993; Bobba 2002).

A major part of the area consists of sandy loams and sandy clay loams. The quaternary sediments occupying the coastal tract and inland river valleys include thick blankets of alluvium, gravel and colluvial deposits, beach sand, kankar, and soils of various types. The rivers are intertwined in the upper floodplain and meandering in the lower floodplain. The distribution patterns of calcium and magnesium are mostly controlled by the amounts of shell fragments and clay minerals, particularly montmorillonite (Seetaramaswamy & Poornachandra Rao 1975). The coastal alluvium has varying thicknesses in different areas, and includes a number of sand beds in which groundwater is present in a confined condition. The area is represented by tidal flats, inlets which receive seawater during high tides. The thickness of granular zones in the alluvium ranges from 18 to 258 m within the explored depths (CGWB 1999; GSI 2006). The hydrogeophysical investigations in the study area indicated that loamy sandy soils are underlined by thick clay beds of about 18–25 m followed by coarse sands (Gurunadha Rao *et al.* 2011, 2013; Naidu *et al.* 2012; Surinaidu *et al.* 2014).

The Godavari delta area is a flat alluvial terrain and ground elevations vary from ~2 m at the Ravva onshore terminal near the coast to a maximum elevation of 7 m from the mean sea level observed at Amalapuram on the western side. The area experiences seasonal floods in every alternate year through the Godavari River, during the study period sequential floods occurred in 2006 (Gurunadha Rao *et al.* 2011). The Godavari irrigation canal network is well spread out in the area and provides a perennial source of irrigation in all seasons. Irrigation canals in the area flow towards the Bay of Bengal through three important drains – Vilastippa, Kunavaram and Pikaleru. Kunavaram and Pikaleru drains pass through the Ravva onshore terminal area. The freshwater aquaculture farming is one of the major land use practices using surface water sources in the central Godavari delta. The canals have been in operation throughout the last century and contribute to groundwater recharge. This has an impact on the groundwater quality in the area. The elevation of the water table is around 3 m (amsl) in the Godavari alluvium. Fluctuations of the water level from pre-monsoon to post-monsoon is generally within 0.5 m except in some localized pockets in the delta where it is about 2.5 m (CGWB 1999).

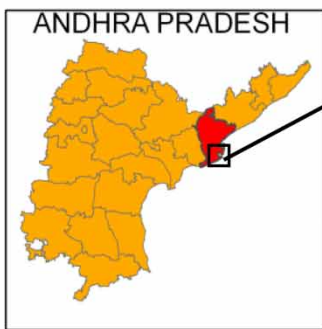
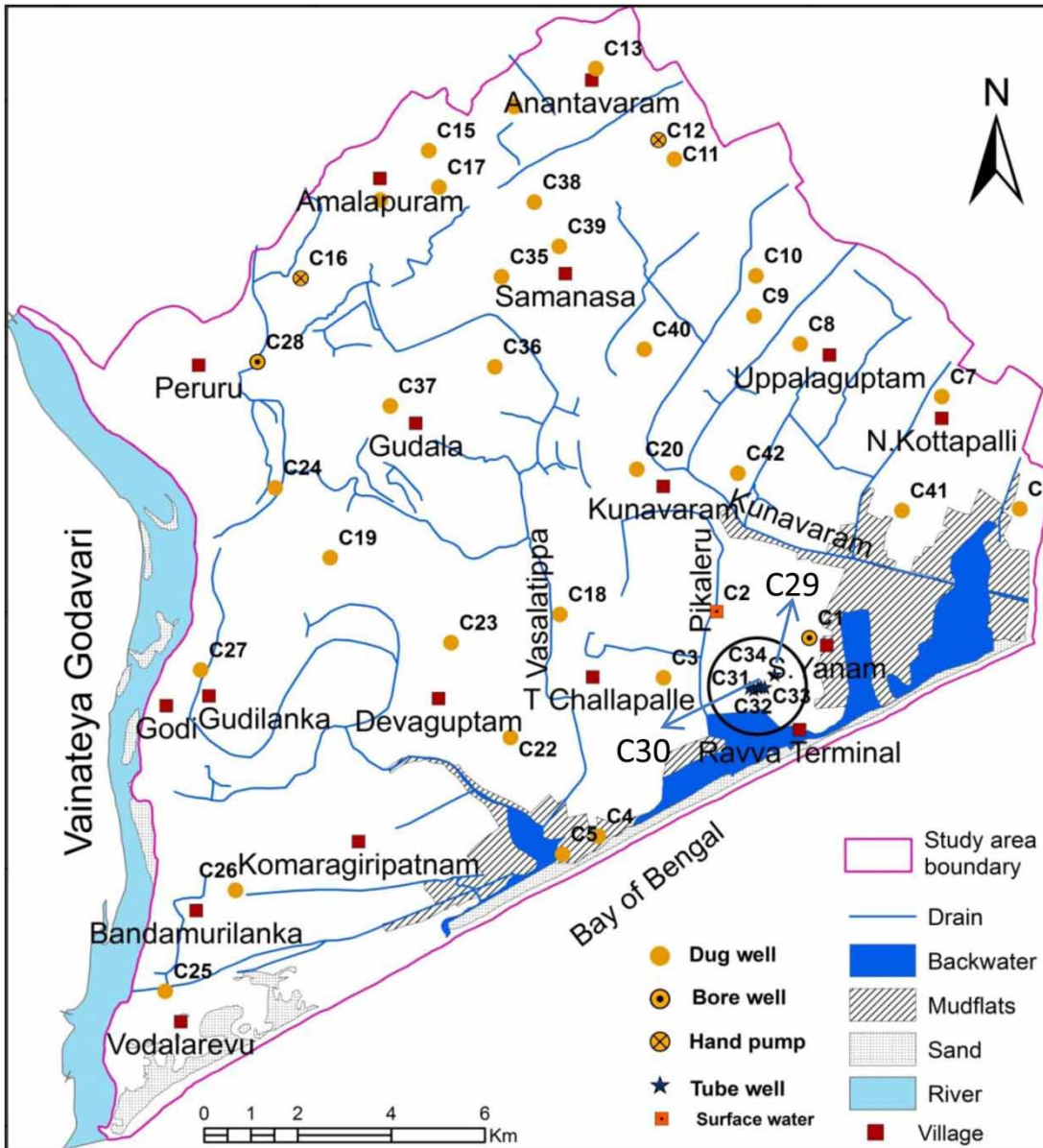


Figure 1 | Location of the study area and observation wells in the central Godavari delta.

METHODOLOGY

Major ions

For the assessment of groundwater quality, 36 groundwater samples were collected in the pre- and post-monsoon periods of 2006. The analyses results indicate the established observation wells are not sufficient to understand hydrochemical dynamics due to hydrogeological heterogeneity upstream of the area. Hence, the number of samples was increased to 42 to cover the entire area in 2007. The locations of monitoring wells are shown in [Figure 1](#). Samples were collected and analyzed for major ions (pH, electrical conductivity (EC), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), fluoride (F^-), bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-)) by following standard methods suggested by [APHA \(2005\)](#). Ca^{2+} , Mg^{2+} , HCO_3^- , CO_3^- and Cl^- are analyzed by the volumetric method; Na^+ and K^+ are analyzed by flame photometer; F^- is analyzed by ion metric methods; NO_3^- by double beam spectrophotometer; SO_4^{2-} by turbidity; pH by a pH meter; and total dissolved salt by gravimetric method and conductivity meter.

Stable oxygen isotope ($\delta^{18}\text{O}$)

In the study area, groundwater samples were collected in the deep wells located in and around Ravva Onshore Terminal to identify the source of salinity and to understand the mixing process of saline and fresh waters in three seasons (November 2006, November 2007 and June 2008). Oxygen isotopes in 13 samples are measured using mass spectrometry. The methodology to measure $^{18}\text{O}/^{16}\text{O}$ ($\delta^{18}\text{O}$) is well explained by [Epstein & Mayeda \(1953\)](#). Oxygen isotope compositions are commonly reported relative to an agreed sample of ocean water, referred to as the Standard Mean Ocean Water (SMOW), representing the largest and most equilibrated water body. Stable isotope ratios ($^{18}\text{O}/^{16}\text{O}$) of water are conventionally expressed as units of parts per thousand (per mil ‰) deviation from SMOW. Vienna Standard Mean Ocean Water (VSMOW) standard was used for oxygen isotope analyses of water samples ([Gonfiantini 1978](#)).

$$\delta^{18}\text{O}_{\text{V-SMOW}}(\text{‰}) = \left(\frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} - 1 \right) \times 1000$$

Multivariate statistical approach

Factor analysis

Factor analysis is a multivariate statistical technique that can be utilized to examine the patterns or relationships of a large number of variables and summarize information in a smaller set of factors or components to predict behavior ([Davis 2002](#)). R-mode factor analysis has proven highly effective in studies of groundwater quality and provides several positive features that allow the interoperation of data ([Subbarao et al. 1995](#); [Reghunath et al. 2002](#); [Rao et al. 2005](#)). The most important feature of factor techniques is their ability to reduce a large number of variables down to a smaller number of factors to produce new combinations of original variables (groups) that can then be used as new variables in some further analyses. Many researchers have successfully applied factor analysis to interpret various hydrochemical processes ([Ruiz et al. 1990](#); [Papatheodorou & Lambrakis 1997](#); [Voudouris et al. 2000](#); [Lambrakis et al. 2004](#); [Panagopoulos et al. 2004](#); [Shrestha & Kazama 2007](#); [Zhou et al. 2007](#); [Koklu et al. 2010](#)). In the present study the principal component (PC) method is used for the initial factor extraction and the Varimax method is used for factor rotation using Software Package for the Social Science (SPSS) software ([Landau & Everitt 2004](#)).

Cluster analysis

Cluster analysis is a statistical tool used to classify the data according to their similarities. A small squared Euclidian distance implies a high similarity between measured objects. In clustering, the distinct groups can reveal either the interaction among the variables (R-mode) or the interaction among the samples (Q-mode) ([Wu et al. 2005](#)). The Q-mode hierarchical cluster analyses have been performed in the study area using SPSS software ([Landau & Everitt 2004](#)). Ward's clustering procedure ([Ward 1963](#)), which is commonly used in the hierarchical method of cluster analysis, is employed to identify the cluster of the samples. Various types of cluster analysis have been successfully used to view water-chemistry data for both surface water ([Alther 1979](#); [Güler et al. 2002](#); [Templ et al. 2008](#); [Salah et al. 2012](#)) and groundwater ([Troiano et al. 1994](#); [Farnham et al. 2000](#)).

RESULTS AND DISCUSSION

Hydrogeochemical process

The groundwater is apparently saline and of marine origin, as indicated by its $\text{Na}^+\text{-Cl}^-$ water type (Gurunadha Rao *et al.* 2011; Naidu *et al.* 2012; Surinaidu *et al.* 2013). Large proportions of groundwater are of the $\text{Na}^+\text{-Cl}^-$ water type, which generally indicates a strong seawater influence on the aquifer. In the central Godavari delta, three major hydrochemical facies are identified using the Piper geochemical classification method (Piper 1944). These are: (i) groundwater associated with evaporites (sodium chloride), (ii) groundwater of meteoric origin, and (iii) mixing of saline water and up-coning of brines/salt water (Figure 2). Water samples contain significantly higher proportions of sodium and chloride, which are most likely derived from evaporated seawater and dissolution of evaporites. Groundwater with low major ion concentrations is largely meteoric water with some influence of the mixing of sodium chloride type groundwater. In addition to physical mixing, the up-coning of brackish waters is observed and was indicated by magnesium and calcium dominated water in the Piper diagram. The Piper classification also indicates groundwater quality in the deltaic region was affected by dissolution of evaporates in the post-monsoon of 2006 (Figure 2(a)). It is due to a large number of rainy days and sequential flood events dissolution taking place

in the post-monsoon 2006 (IMD 2006). However, in the post-monsoon of 2007, water samples moving towards meteoric mixing indicated that simple dilution was taking place (Figure 2(b)). This indicates the influence of the mixing of sodium chloride type groundwater by natural recharge and irrigation return flows. However, brackish water pumping wells are shifting to high saline waters/intrusion phase due to up-coning of salt water/seawater intrusion due to large scale groundwater pumping at point location (Figure 2(a) and (b)).

To investigate the importance of the ion exchange process in the groundwater chemistry, the groundwater quality samples are examined to identify the relationship between cations and anions and ion exchange process with X-Y diagrams for pre- and post-monsoon seasons as shown in Figure 3. Figure 3(a) and (b) shows $\text{Na}^+\text{-Cl}^-$ versus $\text{Ca}^{+2} + \text{Mg}^{+2}\text{-SO}_4^{-2}\text{-HCO}_3^-$, indicating that almost all samples are below the 1:1 mixing line which indicates the influence of the ion exchange process (Jankowski *et al.* 1998), but a few of the samples indicate reverse ion exchange in the groundwater pumping wells located near the coast. In Figure 3(c) and (d) the tendency of $\text{N}^+\text{-K}^+/\text{Na}^+\text{-K}^+ + \text{Ca}^{+2}$ approaches a value of 1, with increasing total dissolved solids (TDS), indicating an ion exchange process in the groundwater of the Godavari delta (Figure 3(c) and (d)). The driving force for salinity could be dissolution of evaporites or seawater mixing, when $\text{HCO}_3^- + \text{SO}_4^{2-}$ is less than 5 meq/L, which also indicates that the dissolution

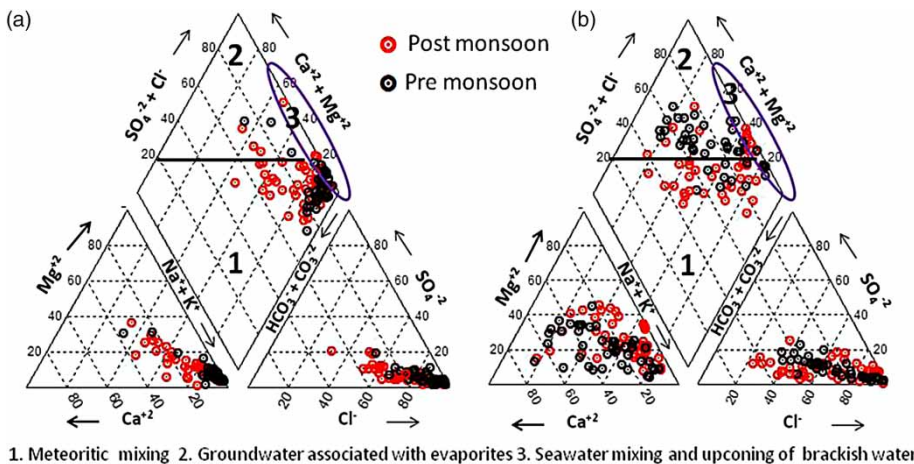


Figure 2 | Piper classification for major ion chemistry explains major hydrochemical process in the central Godavari delta, 2006 (a) and 2007 (b).

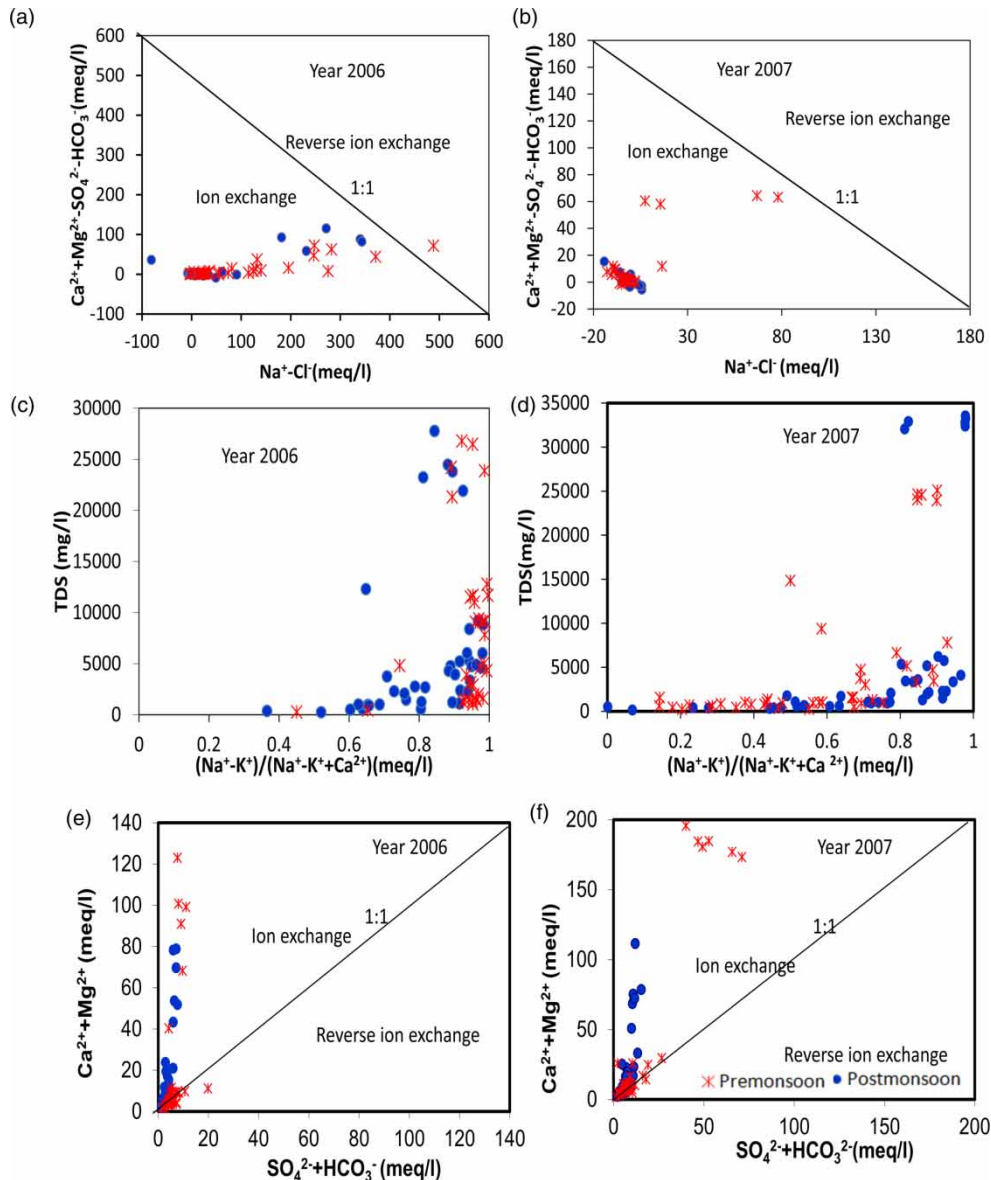


Figure 3 | X-Y diagrams illustrating relationships among the major ions and ion exchange process.

of calcite and dolomite is the major process influencing the water chemistry (Kalantary *et al.* 2007). However, almost all samples from the Godavari delta lie under the ion exchange process and $\text{HCO}_3^- + \text{SO}_4^{2-}$ is less than 5 meq/L, indicating an ion exchange and gypsum dissolution process, and it is high in the deep pumping wells (Figure 3(e) and (f)). It also indicates that seawater mixing and dissolution of evaporites are driving factors for increasing salinity in the Godavari delta.

Relation between stable oxygen isotopes ($\delta^{18}\text{O}$) to chloride and groundwater table

The isotopic compositions may vary with the type of water such as seawater, fresh water and a mixture (Ženišová *et al.* 2015). Therefore, groundwater affected by seawater is believed to be enriched in $\delta^{18}\text{O}$ ($^{18}\text{O}/^{16}\text{O}$) as compared to freshwater (Izbicki 1996; Ma *et al.* 2007). In general the seawater will record isotopic ratios close to zero, while the

meteoric waters show negative values (Craig 1961; Jager & Hunziker 1979). The analyzed data shows negative values in all the samples indicating that salinity in the wells does not belong to the recent/current seawater. The weighted mean values of the of $\delta^{18}\text{O}$ close to positive in the Ravva Onshore Terminal wells (C29, C30, C31, C32, C33) indicate mixed waters (mixing of saline water through infiltration from back waters and entrapped sea water in deeper layers of the aquifer system, Table 1). One of the wells (C34) in the Ravva Terminal does not reflect heavier $\delta^{18}\text{O}$ (−2.8 to −2.9) which is observed to be subjected to very low pumping and less percentage of sea water compared to other wells. The wells located near the coast on mudflats (C5 and C6) exhibit depleted values indicating the influence of accumulated rain/recent fresh water in dug wells. Hence, in the 2006 sampling period the samples are highly depleted due to heavy rains and, further, they became marginally enriched in $\delta^{18}\text{O}$ values.

The chloride concentrations and depth to water table compared with $\delta^{18}\text{O}$ (‰) are presented in Figure 4(a)–(d). It can be seen from these figures that $\delta^{18}\text{O}$ (‰) enrichment increased with chloride concentrations ranging from −0.36 to −2.84 in November 2006, to −0.63 to −3.21 in November 2007 for groundwater samples inside Onshore Terminal. On the other hand $\delta^{18}\text{O}$ (‰) varied from −2.54 to −8.67 in November 2006 and −2.12 to −6.17 in November 2007 for wells outside Ravva Onshore Terminal. However, the

isotopic ratio (−1.34) (Pikaleru drain, C2) of canal water indicated evaporation and mixing of recent saline water in November 2007, while in June 2008 the elevated isotopic ratio (−0.98) (Table 1) indicated increased mixing of salt water. Ground water possessing marginally higher isotopic ratios in the C3 well located in the downstream region of the delta near the coast is attributed to infiltration of sea water. Further, the enrichment of $\delta^{18}\text{O}$ (‰) in groundwater with depth is due to palaeo salinity in the deeper parts of the aquifer system. Isotopic ratios of Ravva Terminal wells approaching seawater characteristic values can be attributed to the up-coning of entrapped seawater due to heavy pumping at point location in the Ravva terminal wells. Bhisim Kumar *et al.* (2011) conducted hydrogeologic, hydrochemical and isotopic investigation in the Krishna and Godavari basins to find the salinity source and the results revealed that canals are contributing significant recharge that freshen saline groundwater of Palaeo origin. The high salinity of groundwater is due to dissolution of marine clays of Palaeo origin.

Factor analysis

In the central Godavari delta, groundwater elevations are less than 3 m (89% of the wells), and the elevation is more than 9 m in a few locations (11%) and they are located near the coast and are pumping the brackish water. The groundwater salinity may be due to various factors such as seawater mixing, dissolution of evaporitic minerals or evaporation from groundwater. The factor analysis is applied to identify the major hydrochemical process in the Godavari coastal region. The rotated factor loadings, communalities, eigenvalues and percentage variance associated with factors for principal component analyses (PCA) are presented in Tables 2 and 3. The factor loadings greater than 0.7 are considered as the most important parameters that participate in the major hydrochemical process in the area. From the tables, three factors with represented eigenvalues greater than unity are identified, which account for greater than 80% of the total variance in all the sampling periods of the original dataset.

Factor 1

The factor 1 loadings have explained >50% of variance that includes TDS, SO_4^{2-} , Cl^- , Na^+ , Ca^{+2} and Mg^{+2} are major

Table 1 | $^{18}\text{O}/^{16}\text{O}$ values in the central Godavari delta, East Godavari district, A.P.

ID	November 2006	November 07	June 2008
C2	–	−1.34	−0.98
C3	−0.98	−0.89	−0.17
C4	−5.47	−4.94	−3.89
C5	−4.12	−3.97	−3.12
C6	−6.49	−6.12	−5.13
C18	−8.67	−5.17	−3.97
C22	−2.54	−2.12	−1.92
C29	−0.64	−0.83	–
C30	−0.64	−0.88	−0.96
C31	−0.48	–	−0.93
C32	−0.36	−0.63	−0.74
C33	−0.45	−0.59	−0.85
C34	−2.8	−3.21	−2.96

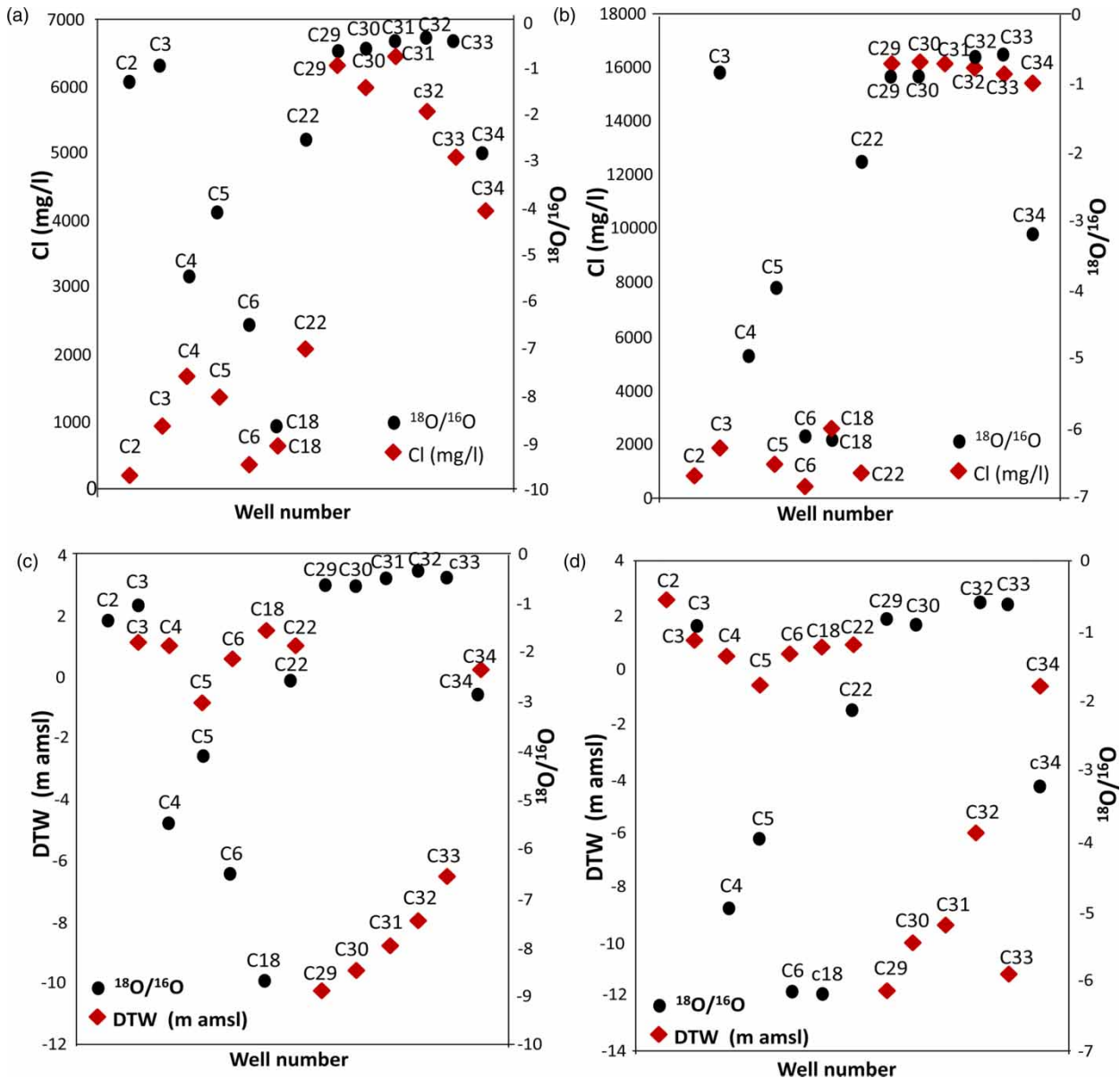


Figure 4 | The relation between $^{18}\text{O}/^{16}\text{O}$ versus chloride in November 2006 (a) and November 2007 (b), depth to water level in m (amsl) versus $^{18}\text{O}/^{16}\text{O}$ in November 2006 (c) and November 2007 (d).

parameters driving salinity in the area. These factors have factor scores greater than 0.8 (Table 2). Therefore, factor 1 associated with these parameters resulted from a strong influence of sea water mixing and dissolution of aquifer matrix in the groundwater. The mixing of saline water can control the concentrations of magnesium, calcium and sulphate. The dissolution of evaporates are the most important process affecting the ionic concentrations of water in the aquifer,

as this factor accounts for greater than 50% of the variance of the concentrations of the samples in all sampling periods (Tables 2 and 3), which is a much higher percentage than that attributable to the other factors. However, in post-monsoon 2006, K^+ also contributes as a major constituent in addition to TDS, SO_4^{2-} , Cl^- , Na^+ , Ca^{+2} and Mg^{+2} loadings which influence the groundwater quality (Table 2). It is evident that potassium is increased due to

Table 2 | Factor scores and communalities for pre- and post-monsoon of 2006

Parameter	Pre-monsoon 2006				Post-monsoon 2006			
	Factor 1	Factor 2	Factor 3	Communalities	Factor 1	Factor 2	Factor 3	Communalities
pH	-0.803	0.26	0.352	0.836	-0.259	0.638	-0.501	0.724
TDS	0.956	0.17	0.17	0.971	0.979	-0.088	-0.007	0.966
HCO ₃ ⁻	-0.167	0.889	-0.092	0.827	0.071	0.81	0.187	0.695
Cl ⁻	0.893	0.004	0.283	0.877	0.95	-0.14	-0.031	0.923
F ⁻	0.077	0.157	0.882	0.809	0.235	-0.709	-0.158	0.583
NO ₃ -N	-0.174	0.297	-0.546	0.416	-0.066	0.259	0.858	0.807
SO ₄ ²⁻	0.963	-0.053	0.041	0.932	0.961	-0.111	0.099	0.946
Na ⁺	0.891	0.252	0.299	0.946	0.974	-0.119	-0.036	0.965
K ⁺	0.487	0.644	0.104	0.802	0.911	0.05	0.129	0.849
Ca ²⁺	0.826	-0.206	0.241	0.783	0.882	-0.189	-0.068	0.818
Mg ²⁺	0.876	0.138	0.048	0.789	0.807	-0.159	-0.04	0.678
Eigenvalues	5.826	1.681	1.481		6.125	1.749	1.082	
% of variance	52.966	15.286	13.461		55.681	15.9	9.835	
Cumulative %	52.966	68.252	81.713		55.681	71.581	81.416	

Table 3 | Factor scores and communalities for pre- and post-monsoon of 2007

Parameter	Pre-monsoon 2007				Post-monsoon 2007			
	Factor 1	Factor 2	Factor 3	Communalities	Factor 1	Factor 2	Factor 3	Communalities
pH	-0.719	0.349	-0.209	0.682	-0.579	0.206	0.606	0.745
TDS	0.976	0.129	0.095	0.978	0.956	0.075	-0.267	0.992
HCO ₃ ⁻	0.215	0.892	0.046	0.845	0.719	0.26	-0.032	0.586
Cl ⁻	0.979	0.066	0.081	0.969	0.954	0.053	-0.276	0.988
F ⁻	0.024	0.26	0.768	0.659	-0.116	0.017	0.948	0.913
NO ₃ -N	-0.146	0.189	-0.764	0.641	-0.095	0.932	0.007	0.878
SO ₄ ²⁻	0.967	0.115	0.028	0.949	0.954	0.151	-0.201	0.974
Na ⁺	0.97	0.02	0.073	0.946	0.956	0.074	-0.26	0.988
K ⁺	0.82	0.397	0.094	0.839	0.372	0.851	0.095	0.871
Ca ²⁺	0.862	0.231	0.148	0.819	0.717	-0.062	0.212	0.563
Mg ²⁺	0.883	0.16	0.047	0.808	0.904	0.074	-0.372	0.961
Eigenvalues	6.565	1.293	1.275		5.993	1.749	1.717	
% of variance	59.685	11.755	11.592		54.484	15.902	15.608	
Cumulative %	59.685	71.44	83.031		54.484	70.386	85.994	

the breakdown of clay mineral resulting from the dissolution process due to heavy rainfall and flood events in this period. The factor scores indicate that the same influence has continued in the pre-monsoon 2007 period whereas in the

post-monsoon 2007 period the relative decrease in these loadings and no influences of K⁺ loading on factors scores indicates the dilution process in the aquifer system from rainfall recharge (Table 3). The spatial and temporal

distribution of factor scores for factor 1 for each of the sampling periods is shown in Figure 5. It can be seen from Figure 5(a)–(d) that the coastal groundwater pumping wells are characterized by particularly high scores. The

high scores are attributed to close proximity to the sea, as a consequence of the intrusion of seawater either directly from the sea or upcoming of saline water due to heavy pumping at point source locations from Ravva terminal

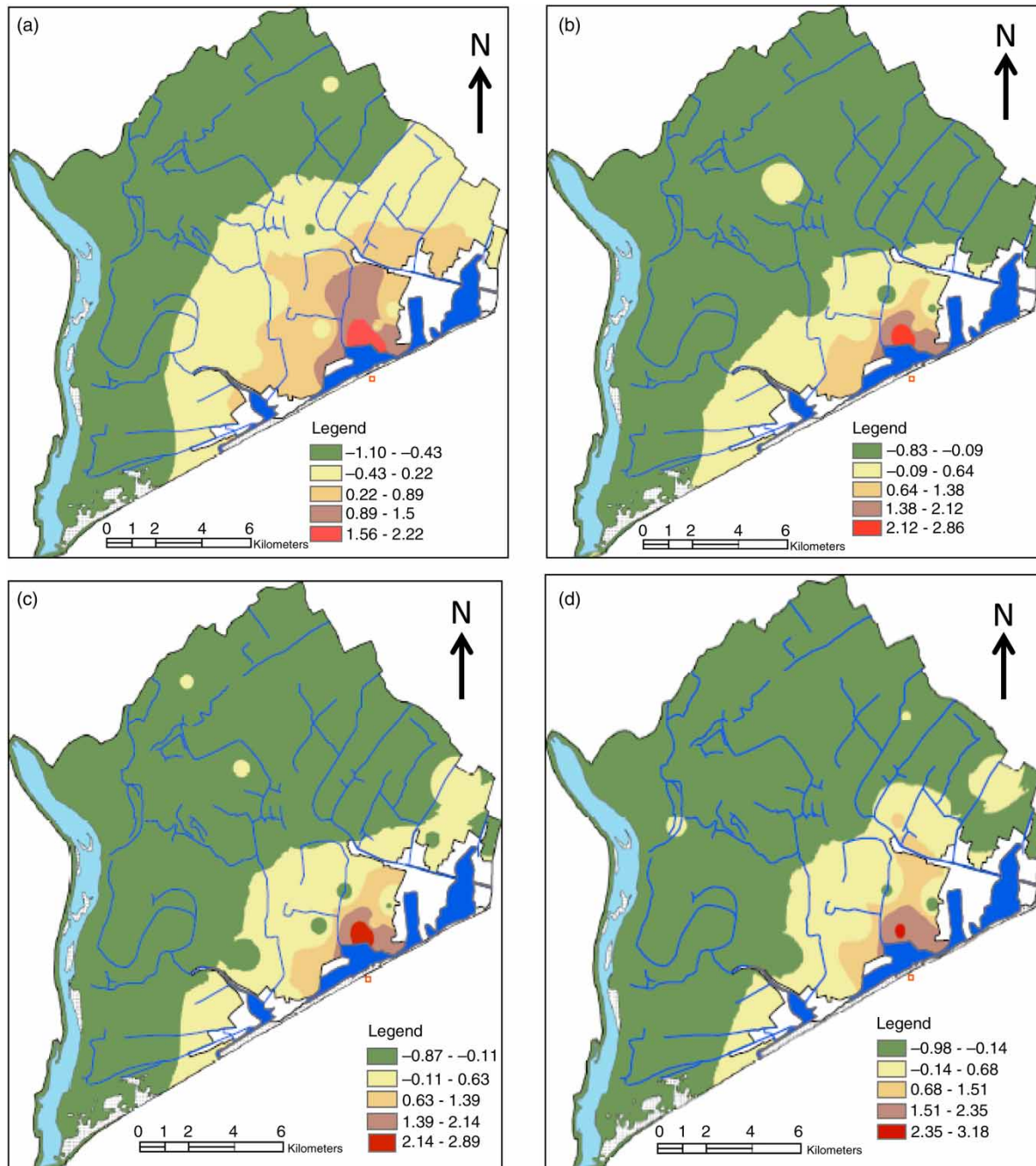


Figure 5 | Spatial distribution of factor scores for factor 1 from 2006 to 2007, pre-monsoon 2006 (a), post-monsoon 2006 (b), pre-monsoon 2007 (c), post-monsoon 2007 (d).

wells. The gradual increase in factor loadings in and around these pumping wells indicates an increase in the mixing of saline water with groundwater due to excessive withdrawals of groundwater. The negative loadings of pH, HCO_3^- and NO_3^{2-} indicate relatively no influence of these factors on the groundwater.

Factor 2

Factor 2 accounts for 15.2% of total variance in all sampling periods except June 2007, and it is mainly associated with very high loading of bicarbonates and pH (Tables 2 and 3). The high bicarbonate loadings may be the result of dissolution of CO_2 in the water due to the influence of rainwater recharge (Lawrence & Upchurch 1982) and dissociation of

the H_2CO_3 formed ($\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HCO}_3^-$), which increases the H_3O^+ and HCO_3^- concentrations. The positive loadings of pH may be attributed to an increase in bicarbonates which resulted in an increase in pH.

Factor 3

This factor accounts for 11.5% of variance in the pre-monsoon period of 2006 and 9.85% of the variance in the post-monsoon period. In 2007, the percentage variance varies from 11.5 to 15.6% from the pre-monsoon to post-monsoon period. In factor 3, high positive loadings of fluoride in the pre-monsoon period and nitrate loadings in the post-monsoon period is observed (Tables 2 and 3). The presence of high fluoride concentrations may be

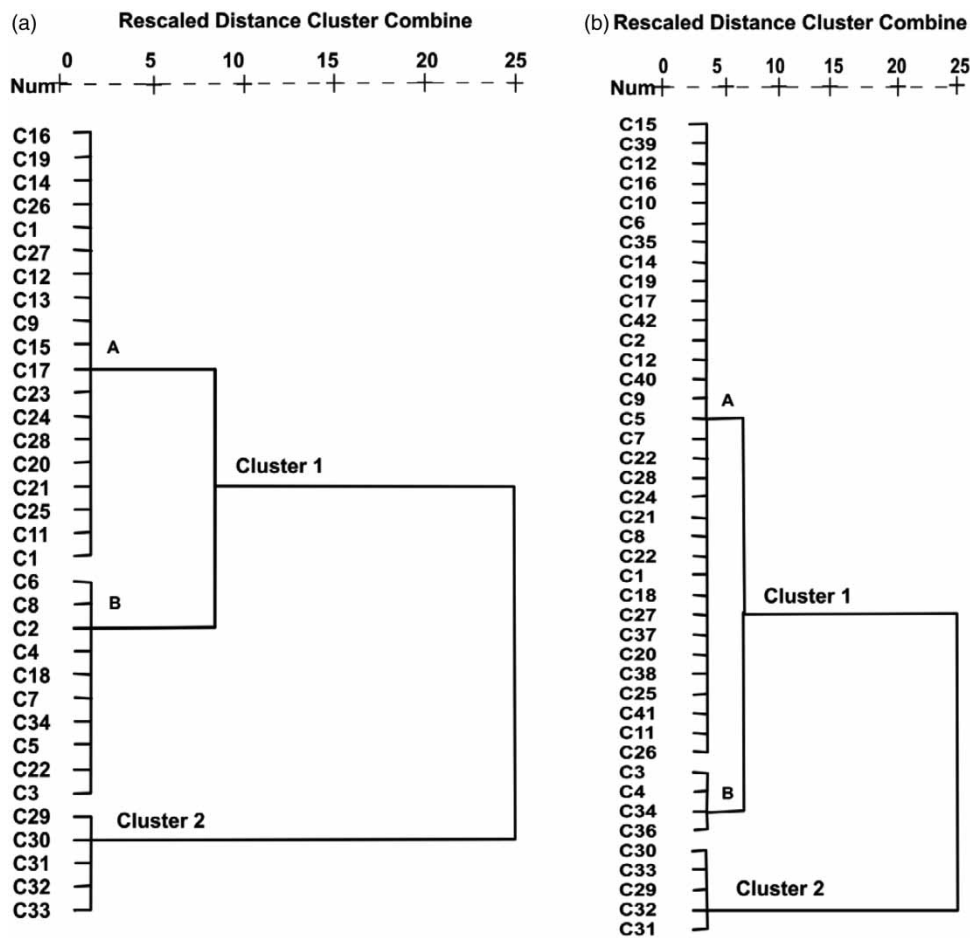


Figure 6 | Dendrogram of the hierarchical cluster analysis of the groundwater quality of the central Godavari delta using complete linkage method, (a) pre-monsoon 2006 and (b) post-monsoon 2006.

attributed to the dissolution of phosphate fertilizers applied for agriculture at the top of the aquifer. In the post-monsoon period, the nitrate loadings are increased. This is due to leaching of agricultural inputs and aquaculture farming applied to the top of the aquifer. However, in the post-monsoon period negative loadings of fluoride indicated a dilution process.

Cluster analysis

Cluster analysis consists of a series of multivariate methods which are used to group similar objects/samples based on similarities of their chemical properties (Danielsson *et al.* 1999). The hierarchical method of cluster analysis, which is used in this study, has the advantage of not demanding

any prior knowledge of the number of clusters, which the non-hierarchical method requires. The analysis has divided the groundwater samples into two major clusters/groups based on hydrochemical variables (pH, TDS and major ions). The grouped clusters for four different seasons are shown in Figures 6 and 7. The descriptive statistics of these clusters are presented in Tables 4–6 which represents ionic concentrations of these clusters and the number of samples that fall in each cluster. Cluster 1A and cluster 1B samples have groundwater depths less than 3 m whereas cluster 2 samples have depths greater than 10 m and tap the deep aquifer from depths of >67 m (Surinaidu *et al.* 2014). Only five samples (11.9% in total) in cluster 2 are identified with relative concentrations of $\text{Na}^+ > \text{Cl}^- > \text{Ca}^{+2} > \text{Mg}^{+2}$ and in the post-monsoon period of 2007 it

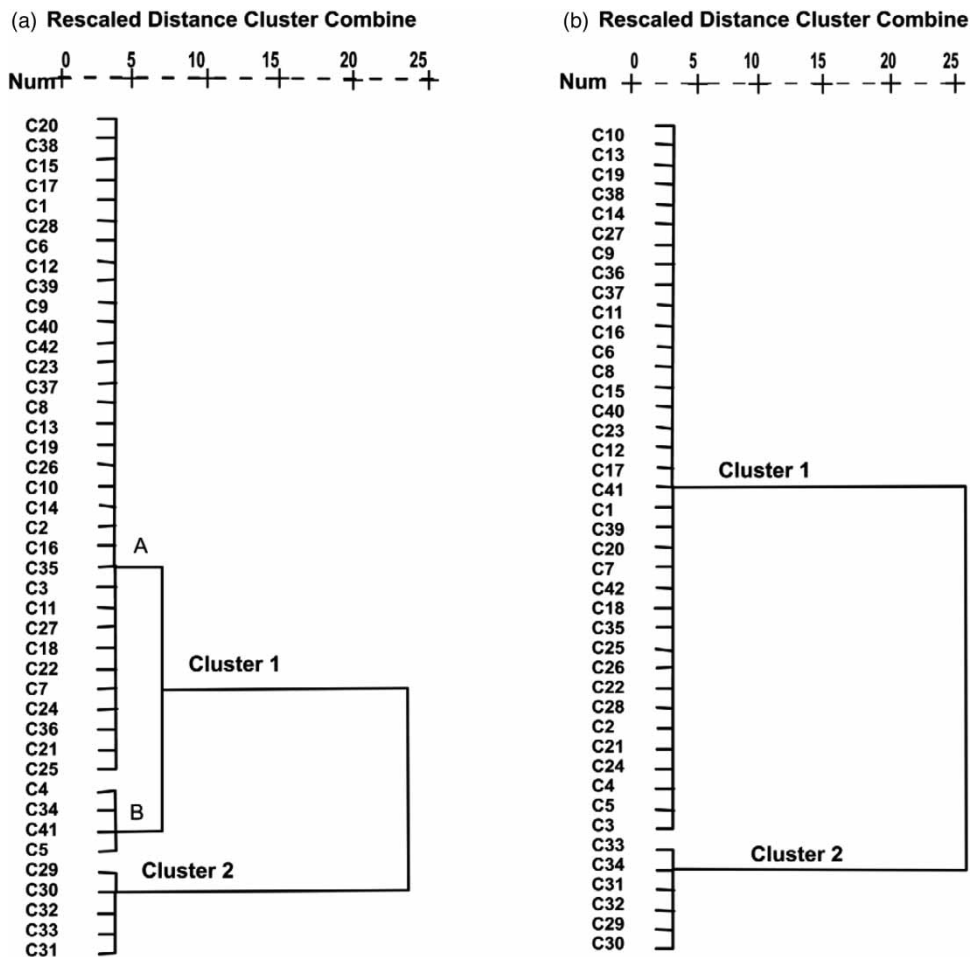


Figure 7 | Dendrogram of the hierarchical cluster analysis of the groundwater quality of the central Godavari delta using complete linkage method, (a) pre-monsoon 2007 and (b) post-monsoon 2007.

Table 4 | Descriptive statistics of major ions in cluster 1A

Parameter	Pre-monsoon 2006			Post-monsoon 2006			Pre-monsoon 2007			Post-monsoon 2007		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	7.9	8.9	8.4	7.5	8.8	8.0	7.5	8.9	8.3	7.1	8.2	7.7
TDS	274	5030	2426	248	6029	2585	256	5146	1598	141	6221	1994
HCO ₃ ⁻	49	195	108	61	390	228	61	542	259	70	850	344
Cl ⁻	57	1334	554	64	2080	715	43	2172	566	19	3301	772
F ⁻	0.38	0.95	0.65	0.32	1.02	0.72	0.37	0.98	0.70	0.07	0.74	0.32
NO ₃ -N	3	81	18	5	99	18	5	81	15	0.05	209	33
SO ₄ ²⁻	20	60	36	30	140	60	30	135	71	11	610	129
Na ⁺	24	2553	1023	32	2118	564	12	880	244	6	1629	465
K ⁺	2	632	169	2	378	83	2	164	33	5	336	57
Ca ²⁺	12	80	37	24	96	50	16	264	99	30	296	78
Mg ²⁺	12	114	45	5	83	36	5	180	59	4	243	79
Sample numbers	N = 21(C1, C9 to C17, C19 to C21, C23 to C28)			N = 33 (C1,2, C5 to C28, C35, C37 To C42)			N = 33 (C1 to C3, C5 to C28, C35 to C40, C42)			N = 36 (C1 to C 28, C35 to C42)		

Table 5 | Descriptive statistics of major ions in cluster 1B

Parameter	Pre-monsoon 2006			Post-monsoon 2006			Pre-monsoon 2007		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	7.40	8.70	8.08	8.00	8.10	8.05	8.00	8.60	8.23
TDS	7827	12768	10320	8390	12301	9906	6643	14848	10028
HCO ₃ ⁻	73	220	142	159	1037	515	244	610	455
Cl ⁻	299	2985	1457	973	4142	2673	2982	3990	3457
F ⁻	0.25	0.85	0.57	0.44	0.96	0.65	0.64	1.06	0.82
NO ₃ -N	2	30	10	8	17	12	7	10	9
SO ₄ ²⁻	30	210	91	75	135	106	75	180	135
Na ⁺	2829	7590	4849	798	4096	2456	1310	2526	1775
K ⁺	94	803	389	52	562	273	84	275	172
Ca ²⁺	24	184	97	40	360	168	164	1224	644
Mg ²⁺	80	416	181	73	272	144	122	238	168
Sample numbers	N = 10 (C2,3,4,5,6,7,8,18,22,34)			N = 4 (C3, 4, 34,36)			N = 4 (C4,5, 34,41)		

is shifted to Na⁺ > Cl⁻ > Mg²⁺, which occurred as a result of up-coning of saline/salt water intrusion due to excessive groundwater pumping near the coast. The number of samples in each cluster varied in different seasons and the details are shown in Tables 4–6. Four (9.5% in total) samples in cluster 1B are identified with relative concentrations of Na⁺ > Mg²⁺ > Cl⁻, and these wells are affected

by saline water mixing/vertical infiltration during high tide through the surface water drains. These wells are located in mudflats and along the drains, and are always affected by saline water during high tides, deteriorating the groundwater quality.

The number of samples in cluster 1A is 33 (78.5% in total samples) with relative concentrations of Na⁺ >

Table 6 | Descriptive statistics of major ions in cluster 2

Parameter	Pre-monsoon 2006			Post-monsoon 2006			Pre-monsoon 2007			Post-monsoon 2007		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	7.30	7.70	7.56	7.60	7.90	7.73	7.56	7.90	7.71	6.90	7.20	7.05
TDS	21307	26797	24395	21917	27771	24412	21917	27771	24997	32064	33536	32824
HCO ₃ ⁻	61	110	84	98	268	171	84	268	155	284	2008	1073
Cl ⁻	4686	6308	5458	4997	6452	5839	4997	6452	5786	15467	16221	15927
F ⁻	0.70	0.95	0.82	0.85	0.96	0.90	0.82	0.96	0.89	0.05	0.53	0.17
NO ₃ -N	3	5	4	6	8	7	4	8	6	18	23	20
SO ₄ ²⁻	220	285	261	270	330	304	261	330	292	1680	1870	1778
Na ⁺	9143	14260	11237	8062	12008	10089	8062	14260	11140	7069	8019	7613
K ⁺	312	546	412	273	789	568	273	789	522	100	150	120
Ca ²⁺	140	952	638	776	1864	1265	638	1864	1142	148	1408	623
Mg ²⁺	73	596	381	73	803	424	73	803	450	1394	2159	1854
Sample numbers	N = 5 (C 29 to C33)			N = 5 (C 29 to C33)			N = 5 (C 29 to C33)			N = 6 (C 29 to C34)		

Ca²⁺ > Cl⁻ > HCO₃⁻ in the pre-monsoon period and Na⁺ > Mg²⁺ > Cl⁻ in the post-monsoon period. The groundwater quality in cluster 1A is affected by dissolution of evaporites and clay minerals, and evaporation from shallow groundwater resulted in increased salinity. Most of the wells in cluster 1A are located away from the coast.

In the post-monsoon period of 2007, the number of clusters reduced to only two groups. The samples located in cluster 1B are mixed with those in cluster 1A and formed only one cluster of samples due to the flushing and dilution effects after rainfall (Table 4). The minimum, maximum and average values of major ion concentrations are presented for each cluster group in Tables 4–6. This indicates that water quality of the wells of cluster 1A recorded the lowest mean concentrations of cations and anions except for TDS, sodium and chloride. However, in the post-monsoon season of 2006 these concentrations increased as a result of dissolution of aquifer material, while the highest concentration of all parameters (except for fluoride and nitrate) is recorded in wells of cluster 1A. On the other hand, wells in cluster 1B recorded intermediate mean concentrations between cluster 1A and cluster 2. The concentration of chloride, sulphate and sodium is depleted in the post-monsoon season of 2007 due to the flushing effect and dilution after rainfall. However, in the pre-monsoon season, the concentrations had increased due to the mixing of saline water during high tides, since all the wells in cluster 1B are located along the drains and mudflats.

CONCLUSIONS

The groundwater samples from 42 observation wells were collected in four different seasons of pre-monsoon (June) and post-monsoon (October) in the years 2006 and 2007 and analyzed for major ions and stable isotopes ($\delta^{18}\text{O}$) in the central Godavari delta, Andhra Pradesh. Different hydrochemical mixing models, stable isotope ($\delta^{18}\text{O}$) analysis and multivariate techniques were successfully applied for these data sets to identify the salinity source and to understand the hydrogeochemical dynamics in the area. The results of major ion chemistry and hydrochemical mixing models indicated that groundwater salinity in the area is

mainly driven by seawater mixing, evaporation from groundwater and weathering of evaporites such as gypsum, ion exchange process and dissolution of marine clays. The higher proportions of sodium and chloride are derived from evaporated seawater and dissolution of evaporites. Groundwater with low major ion concentrations is largely meteoric water with some influence of the mixing of sodium chloride type groundwater. The depleted $\delta^{18}\text{O}$ values of -2.54 to -8.67 in the wells away from the coast are due to accumulation of rainwater. The enrichment of isotopic concentrations in the groundwater near Pikaleru drain (-1.34) is due to evaporation and mixing of recent saline water. The low $\delta^{18}\text{O}$ values close to zero is driven by up-coning of entrapped salt water of palaeo origin in the deeper part of the aquifer. Groundwater quality across the central Godavari delta region has significant spatial and temporal variations. Shallow wells are more sensitive to variations in water quality as they are closer to the ground surface.

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