



# Assessment of denitrification potential for coastal and inland sites using groundwater and soil analysis: the multivariate approach

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**Abstract** In an effort to determine the reason behind excellent nitrate remediation capacity at Kelantan region, a multivariate approach is employed to evaluate extent to which the influence of sea on soil geochemical composition affect variation pattern of groundwater quality. The results obtained from geochemical analysis of paleo-beach soil in coastal site

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at Bachok revealed multiple redox activity at different soil strata, involving both heterotrophic and autotrophic denitrification. In soil and water analysis, eight of the fourteen hydro-geochemical parameters (conductivity, temperature, soil texture, oxidation reduction potential, pH, total organic carbon, Fe, Cu, Mn,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ) measured using standard procedures were subjected to multivariate analysis. Evaluation of general variation pattern across the area reveals that the principal component analysis (PCA), hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) are in consonance with one another on apportioning three parameters ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and conductivity) to the coastal sites and two parameters (Fe and  $\text{NH}_4^+$  or  $\text{NO}_3^-$ ) to inland sites. The step forward analysis of LDA reveals four parameters in order of decreasing significance as  $\text{Cl}^-$ , Fe and  $\text{SO}_4^{2-}$ , while the two-way HCA identifies three clusters on location basis, respectively. In addition to the significant data reduction obtained, the results indicate that proximity to sea and location/geological-based influence are more significant than temporal-based influence in denitrification. By extension, the research reveals that influence of labile portion of natural resources is explorable for broader application in other remediation strategies.

**Keywords** Denitrification · Coastal site · Groundwater · Multivariate

## Introduction

Nitrate is one of the major nutrients of concern in groundwater pollution posing a health risk condition known as methemoglobinemia (Wongsanit et al. 2015). The heavy use of nitrogenous fertilisers in agriculture activities is observed to be the largest contribution of nitrate in groundwater (Mahvi et al. 2005; Mohamed Azwan et al. 2010; Pu et al. 2014; Suthar et al. 2009). In Europe, it is reported that agricultural input of nitrogen in groundwater reaches 55% (Bouraoui and Grizzetti 2014). However, research on nitrate attenuation conducted on different coastal regions with similar activities (farming and fertiliser application) revealed divergent results, suggesting possible influence of hydro-geochemical matrix on the attenuation process. For example, nitrate concentration in coastal aquifer of Daweija in China reached as high as 521 ppm (Han et al. 2015), while that across the coastal aquifer of Kelantan in Malaysia is within the permissible limit (Fauziah et al. 2014; Jamaludin et al. 2013).

Consequent upon the aforementioned, a number of groundwater modelling approaches regarding nitrate pollution have been reported with appreciable degree of accuracy in predicting nitrate attenuation study. Researches that dwells on performance evaluation of nitrate mass transport numerical models (Matiatos et al. 2019) and those that modelled groundwater nitrate exposure (Messier et al. 2019; Wong et al. 2013) are classical examples of recent effort on understanding the multiple impact of nitrate interaction with the environment.

On one hand, the influence of sea water on the geological formation of the soil and hydro-geochemical matrix is evident in many literatures (Feher et al. 2018; Ishaq et al. 2013; Kefu and Tegu 2009; Koopmans 1972; Raj et al. 2007; Roslan et al. 2010; Wang and Jiao 2012). For instance, the discovery of pyrite-bearing acid soil and reported interface of fresh and saltwater within coastal zones indicate inevitable influence of multiple factors on the quality of water and soil around sea (Roslan et al. 2010; Samsudin et al. 2008). Consequently, the influence of sea on soil geochemical composition lies on its contribution to soil formation when the soil was under water (Kefu and Tegu 2009). This is attested by the Fe-based mineral across the plain, believed to be deposited by sea inundation (Enio et al. 2011; Roslan et al. 2010). Paleo-beach soils are associated with these changes, which

influences the redox condition of groundwater within their zones and hence its quality.

The process of soil formation in the area under study is reported to be podzolisation, wherein different horizons are formed and influenced by immobilisation of Fe and biodegradation of organic acids (Roslan et al. 2010). Excessive sand fraction (95–98%) and presence of pyrite-like sediments reported along the plain support the conclusion that vast area was under the sea in the past (Ishaq et al. 2013). Moreover, Zakaria (1975) attests to the influence of external fluvial and marine forces on the dynamic geomorphology of the Delta. These observations prompt multiple efforts of research in the coastal region.

The coastal plain of north-eastern part of Peninsular Malaysia is an attractive area for research with a strategic geological significance (Enio et al. 2011; Heng et al. 2006; Koopmans 1972). The sedimentary settings of the plain were observed to have been largely influenced by transgressions (Wang and Jiao 2012). Research conducted in the area includes performance of BRIS (beach ridges interspersed with swales) soil, sandy beach ridges, salinity mapping, geomorphology, water quality, hydro-geochemistry and hydro-geochemical studies (Hussin et al. 2016; Ishaq et al. 2013; Jamaludin et al. 2013; Roslan et al. 2010; Samsudin et al. 2008; Sefie et al. 2015; Zakaria 1975). A research conducted at agricultural rural areas of Kelantan reported that no violation of nitrate is detected in all the area (Fauziah et al. 2014; Jamaludin et al. 2013). This conclusion is reached in cognisance with the maximum permissible limit of  $\text{NO}_3^- \text{-N}$  ( $7 \text{ mg L}^{-1}$ ) set by the National Water Quality Standards for Malaysia (Al-Badaii et al. 2013). Also, by screening groundwater through monitoring wells across the region for 13 years, the Minerals and Geoscience Department of Malaysia (MGD) recorded a wide range of varying results that span across different geological matrix. The results indicated mild deviation of nitrate concentration from the maximum permissible limit in the area. Considering the frequent usage of nitrogen-based fertiliser in the area, this successive report necessitates the need for understanding why there is such wide divergent hydrological manifestation in the area. It is therefore imperative to investigate the fate of nitrate in the area and find out the environmental factors (geological, spatial or temporal) that influence such denitrification potential.

Despite the above conspicuous need, it is however observed that most of the research in the area was

focused on pattern recognition, source identification and geochemical evolution. It is therefore clear that less attention is given to the excellent denitrification capacity of the area, let alone the synergistic contribution of hydro-geochemical impact on soil formation to the attenuation process, which is considered in this study. It was established that delta formation in the area is affected by marine influence (Sefie et al. 2015). In addition, recent work has attributed high denitrification potential of a site to its proximity to redox line with high concentration of iron-embedded mineral FeS (in form of pyrite) and Mn (Roy et al. 2017). To the best knowledge of the researchers, no research work has been reported on the dynamic parameters that might influence the good attenuation behaviour in the area. More so, no research has been reported on exploring the geological properties of the area that might be exploited for remediation purposes.

This research proposes to investigate the possible sources of variation pattern and identify the most influential parameters in determining the temporal and spatial hydro-geochemical changes. Multivariate analysis is utilised to evaluate the impact of sea-influenced soil on the variation pattern of groundwater quality. The results obtained at the coastal region are compared with the results obtained at the inland region—whose soil is not reported to be influenced by sea during its formation.

In this study, special emphasis is given to proximity of the sampling point to the South China Sea. This, as observed by researches, has influence on the quality of groundwater (Alberto et al. 2001; Sefie et al. 2015). The selection of the sampling locations is governed by the fundamental quests of finding the influence of the soil formation/condition on denitrification potential (Roy et al. 2017). The objectives of this study are (1) to investigate the influence of geological features of paleo sandy beach (based on the formation) on nitrate attenuation capacity within the coastal plain, (2) to determine the variation/concordance of results within a sampling site taken at different period (temporal) and those at different location taken at the same period (spatial) and (3) to determine the significant parameters responsible for temporal and spatial variations of groundwater quality.

## Materials and methods

Detection parameters used to illustrate the potentials of denitrification in soil and water include nitrate and

nitrite as the main interchangeable nitrogen specie in denitrification, Fe and Mn as inorganic electron donors in both water and soil. In addition, organic carbon and Cu are considered as organic electron source and catalyst in soil, respectively. The following are the materials used and the methods employed.

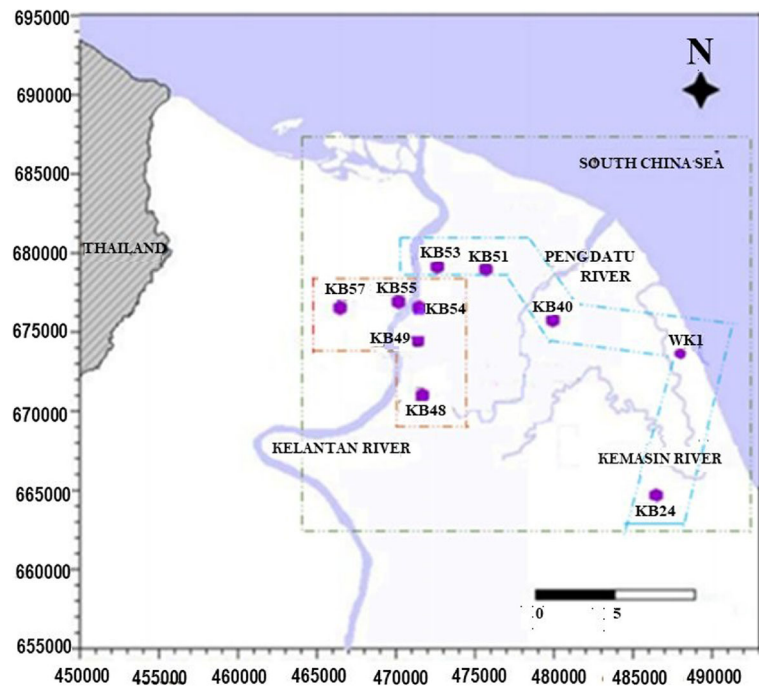
### The study area

Figure 1 indicates the study area (5.98°–6.20° N; 102.16°–102.34° E) which stretches from Bachok (North East) to Kampung Sungai Keladi (North) to Wakaf Bharu (North West) extending to Pasukan Bomba Sukarela (South East). The seasonal distribution is mapped by Azlan et al. (2012) with identification of 3 months of maximum rain fall (November, December and January) 2 months of pre-monsoon (August to September) 2 month of monsoon (November to December) and 5 months of dry season (March to July). However, the northeast monsoon is reported to stretch from October to March (Tang 2019). In order to explore the potential influence of sea on denitrification, the sampling sites were segmented into two categories according to their geographical locations, i.e. the coastal (the sampling well located < 10 km from the shore) and inland (the sampling well > 10 km from the shore). Based on some scientific reports, the influence of sea could reach several kilometres beyond the shoreline where paedogenic pyrite sediments were found (Enio et al. 2011; Ishaq et al. 2013). Moreover, this also have been evidenced by the occurrence of ridges (up to 4 km away) parallel to the shore (Roslan et al. 2010) and interface of salt and fresh water several kilometres away from the shore (Samsudin et al. 2008).

### Sampling

The soil samples were collected from Bachok at three sampling points, all located less than 1.5 km from the shore. Briefly, the soils were sampled at depth interval of 15 cm, and composite samples were blended from individual soil layers in order to mitigate the effect of heterogeneity (Enio et al. 2011).

Water samples were drawn seven times from the sampling wells in both wet and dry season in accordance with the procedures described by Mansor et al. (2012). For elemental analysis, the water samples were preserved with HNO<sub>3</sub> in polyethylene bottle and kept in a

**Fig. 1** Sampling sites

cold box. Similarly, composite sample was used to represent each sampling site.

#### Data collection

The datasets were derived from the following two sources: (1) the field and laboratory analyses of samples from three sampling sites at Bachok, and (2) records from periodic monitoring of wells distributed across the region by MGD.

#### Field measurements

Parameters measured on-site (with the aid of field metres) include ORP, pH, temperature, conductivity and ammonium.

#### Laboratory procedures

The laboratory procedure consists of tests conducted using standard methods as illustrated below.

#### *Ionic chromatography*

The concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  in water samples and aqueous extract (sonication)

of soil samples were determined using standard procedure of Dionex IC 1200 (Scientific 2012).

#### *Atomic absorption spectrometry*

About 0.5 g of soil samples were digested using aqua regia and microwave-assisted digestion. Fe, Mn and Cu in the resulted solutions were determined with PerkinElmer atomic absorption spectrometer (AAS) 400 (Popescu et al. 2013).

#### *Organic matter content and total organic carbon (TOC)*

The organic matter content of the soil was determined using loss on ignition method (Heiri et al. 2001). The total organic carbon (TOC) in the water samples were measured with SSM-5000A Shimadzu total carbon analyser, while that in soil was obtained by conversion factor of 2.5 from the value of organic matter (Nelson and Sommers 1996).

#### *Qualitative test for denitrifies*

To ascertain the presence of nitrate-reducing bacteria in Bachok soil, Sigma-Aldrich procedure in nitrate reduction test was employed.

### Soil texture

The soil texture was measured using mechanical sieving method (Gee and Bauder 1986).

### Data analysis

The hydro-geochemical dataset was processed with Microsoft® Excel 2010 and multivariate analyses, i.e. principal component analysis (PCA), hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) were carried out by SAS® JMP Pro 12. The three multivariate methods applied are interrelated because factor analysis and cluster analysis have been used to identify the most significant factors in data structure and similarities between the factors. This function is in line with objective 2 and 3 of this research. On the other hand, the ward method is obtained by clustering factor scores from the principal component analysis. Cluster analyses are also used for the simultaneous analysis of physical/chemical variables so as to identify distribution zones with shared chemical hydrogeological characteristics. In this analysis, cluster analysis is used in deducing temporal and spatial variations as expressed in terms of hydro-geochemical regimes.

### Data pre-processing

In accordance with the definition of outliers, in which the influence of a data changes the estimate of the parameter of their group by more than 10% (Ghosh and Vogt 2012), five readings were observed to be critical outliers. Hence, the outlier values were normalised by group average (Troyanskaya et al. 2001) and the obtained average values were applied in the calculation.

### Principal component analysis

PCA on correlation was performed to explore the variation pattern in the dataset. This involves decomposition of the normalised data matrix,  $X$ , into a score matrix,  $T$  and a loading matrix,  $P'$ :

$$X = TP' + E$$

where  $E$  is the residual. The scores describe the samples in PC space while the loadings corresponding to the weights of the hydro-geochemical variables onto those

scores (Koki et al. 2017). Such orthogonal transformation eases the interpretation of the variance of multivariate data under a reduced dimension (Alberto et al. 2001). In this regard, the technique was adopted to investigate the hydro-geochemical variability related to seasonal pollution (Zhang et al. 2009).

### Hierarchical cluster analysis

HCA was carried out to discover the cluttering pattern according to hydro-geochemical properties. In this work, dendrogram was derived from the standardised data using Ward's minimum variance method and squared Euclidean distance (Idris et al. 2017). The distance between  $i$ th and  $j$ th clusters is expressed as follows:

$$D = \frac{\|\mu_i - \mu_j\|^2}{\frac{1}{N_i} + \frac{1}{N_j}}$$

where  $\mu$  is the mean vector and  $N$  donates to the cluster size. The linkage and clustering framed help to reveal the natural variations amongst the samples (Hussin et al. 2016).

### Linear discriminant analysis

LDA model was computed to characterise the samples through optimising the separation between the suggested classes. The distance of a sample from the  $i$ th cluster is measured by Mahalanobis distance as follows:

$$D = \sqrt{(x - \mu_i)' S^{-1} (x - \mu_i)}$$

where  $x$  is the sample vector and  $S$  is the covariance matrix.

## Results and discussion

The wells on the map are denoted by prefix KB and WK, each followed by a numeral suffix, which identify the location of the well as shown on the PCA, HCA and LDA figures. In those figures however, the prefixes are substituted with only two letters, "W" for Wet season and "D" for Dry season (Fig. 1). The following are the results obtained from physical observations and chemometric approach.



## Common geological/environmental factors

The common environmental factors shared by the coastal sampling locations are relative proximity to sea, agricultural activities in or around the site, high-temperature condition, heavy precipitation and presence of sea ridges at different level (Roslan et al. 2010). The soil formation pattern is envisaged to be the same, but the period of formation differs and hence, the record of different soil matrix (Raj et al. 2007). The uniformity of soil formation pattern in terms of its composition ensures distribution of common mineral across the area and hence, similar behavioural pattern is expected. Literature indicates that the Bachok area falls under Metang Gelugor member of Gula Formation, which is a Holocene marine unit (Hussin et al. 2014; Suntharalingam 1983). In such coastal sites, the soil is associated with shallow marine deposition consisting of dead particulate organic materials known as detritus (Biddanda and Pomeroy 1988; Kefu and Tegu 2009). This makes the soil easy target for heterotrophic activity (Ibrahim et al. 2015; Korom 1992).

The in-land sampling site shares the same characteristics of heavy precipitation and temperate condition with the coastal sites except that it falls under geological setting of mixed Pleistocene and Holocene continental deposit. In addition, the dominant source of carbon in the soil is plant fossils (Ishaq et al. 2013) and no influence of sea littoral drift on the soil formation has been recorded. The result of soil texture analysis revealed that the horizontal distribution of soil particle size in the paleo-beach site consist of 90.04% of 69–212  $\mu\text{m}$  soil size, which is categorised by the Canadian Soil Survey Committee (CSSC) under fine sand (Fig. 2). This is envisaged to give it excellent filtration properties because soil particles with fine and uniform diameter dominate the matrix.

The qualitative test of nitrate-reducing bacteria gave positive result before and after adding zinc powder, indicating the presence of partial- and complete-reducing microbial species, respectively (content Qty 2013; Zomorodian et al. 2016).

## Hydro-geochemical variation

Figure 3 shows the bi-plot derived from the PCA where the two components explained about 50.7% of the variance in the data set. Despite clear clustering pattern, the scores seem dispersed towards the direction of PC1 or

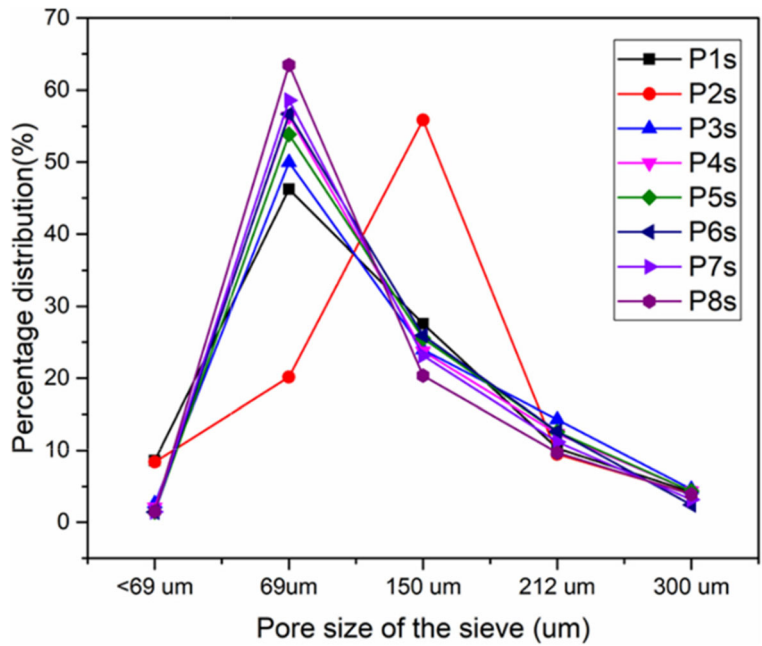
PC2 depending on their hydro-geochemical characteristics that possibly related to their spatial variation, i.e. coastal and inland zones. The loading details as expressed by the Eigen vectors (in Table 1) indicate that conductivity,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  have considerable weights on PC1, Fe and  $\text{NH}_4^+$  on PC2 and pH and  $\text{NO}_3^-$  on PC3. According to the mapping between the scores and loadings,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and conductivity are likely to be associated with samples from coastal zones, while Fe and  $\text{NH}_4^+$  with inland samples. The former is supported by a number of researches around the coastal zones (Hayashi 2004; Jamrah et al. 2008; Sefie et al. 2015), while the latter is in tandem with researches carried in the area (Ahmad et al. 1996; Dasar et al. 2009). However, irregular trend was observed for the borderline sample that originated from the regions between coastal and inland, i.e. sampling well no. 53, with dominance in conductivity and  $\text{SO}_4^{2-}$ , particularly during the dry season. The location of the well within a build-up area and industrial complexes suggests anthropogenic impact. Subsequently, elevated concentration of  $\text{NO}_3^-$  at Well W54 is attributed to anthropogenic inputs for the same reason.

pH tends to be a strong factor in, PC3 but its insignificant Eigen vector in PC1 and PC2 shrinks its loading and hence, not considered. Sampling well W48 at the up-gradient position is influenced by high loading of Fe in wet season (average 14.8 ppm), indicating the dissolution impact of the season on the iron-rich site on inland region. This process is reported by previous studies (Ishaq et al. 2013; Kamal and Hashim 2014; Roslan et al. 2010).

The canonical plot (Fig. 4) of LDA shows the same pattern as PCA. The model revealed four characteristic parameters in order of decreasing significance as conductivity < Fe <  $\text{SO}_4$  < Cl respectively, which supports the decision of disregarding pH as discussed above.

The two-way HCA dendrogram (Fig. 5) reveals three significant hydrochemical facies (clusters). The first one is intersecting cluster (Fig. 5a), comprising of wet season for coastal sample WK1, W24 and inland sample W54 measuring in  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and Fe. The observed intersect may be justified by high chloride and Fe in sampling well W54 (as indicated in the biplot). The second cluster consists of mixed season dominated by in-land upstream wells (W/D48) and downstream well (W57), while the third cluster consists of a downstream mixed season of coastal wells that are situated at the borderline and within industrial zone. This division shows less significant influence of season and more

**Fig. 2** Soil distribution pattern across the layers

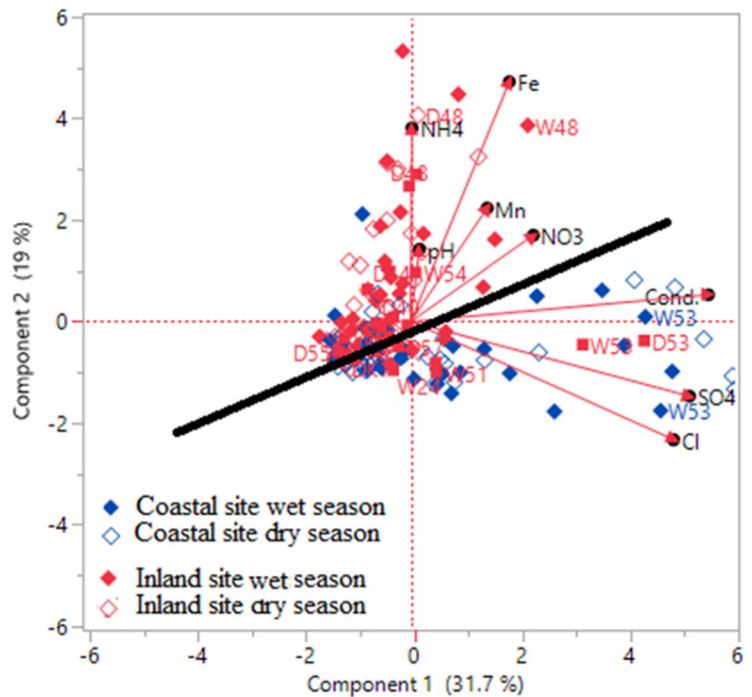


influence of location and activity-induced variation within the site. Hence, the results of PCA, DA and HCA (clusters (b) and (c)) are in concordance on classifying the parameters based on the location and identifying the most influential in each location.

Seasonal (temporal) variation

The seasonal phase was formed by pairing data of different season (wet and dry) obtained from the same site (i.e. either coastal plain site or inland site). The

**Fig. 3** Bi-plot for the general variation



**Table 1** Eigen vectors of the general data

	Prin1	Prin2	Prin3
pH	0.01679	0.19269	0.64392
Cond.	0.57705	0.07191	0.04894
Fe	0.19114	0.63882	-0.00530
Mn	0.14847	0.30277	-0.08416
NH <sub>4</sub> <sup>+</sup>	0.00236	0.51624	-0.54262
Cl <sup>-</sup>	0.50953	-0.31468	-0.12094
SO <sub>4</sub> <sup>2-</sup>	0.54040	-0.19867	-0.14847
NO <sub>3</sub> <sup>2-</sup>	0.23768	0.23010	0.49473

following chemometric tools are used to gauge the variation pattern.

#### Principle component analysis (PCA) – Seasonal

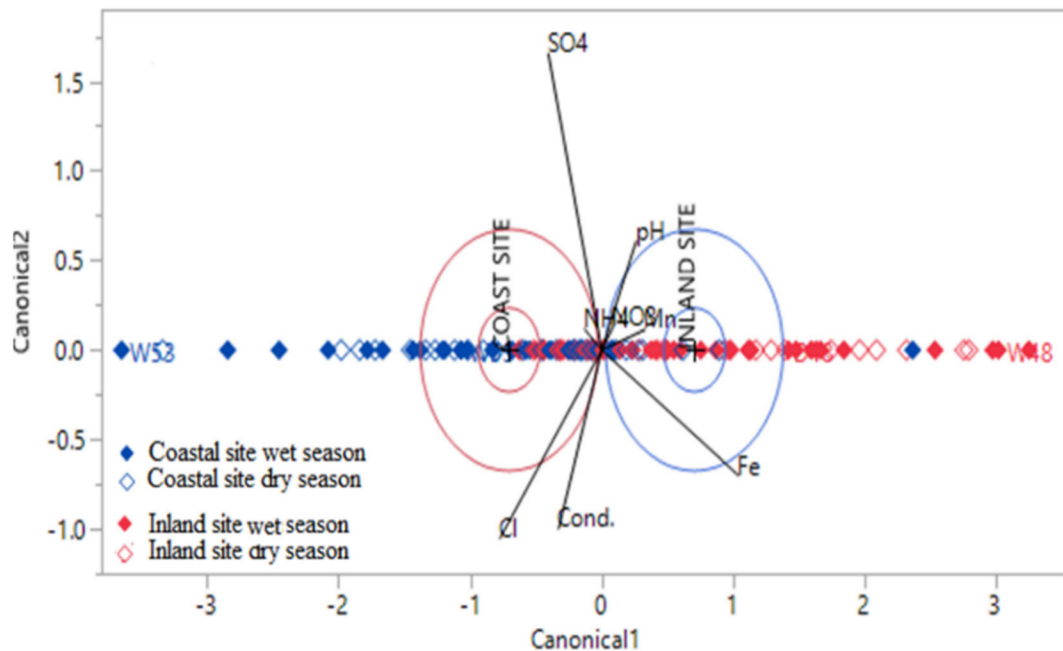
Figure 6a and b show the bi-plot of the variables in inland and coastal sites across the seasons, respectively. Though neither of the patterns of distribution allow for a sharp dividing line between the seasons, conductivity features as a significant factor in each site. Within inland site, the Eigen values revealed high loading of Fe in PC1, suggesting the abundance of Fe-bearing minerals in the area. This trend is reported by Kamal and Hashim (2014); Roslan et al. (2010); Tosi et al. (2009). Also, the

significant loading of ammonium in PC1 shows the presence of ammonium-bearing substrates (fertilisers) in the area and, for the same reason, NO<sub>3</sub><sup>-</sup> becomes significant parameter in PC3.

The mineral dissolution process (Hussin et al. 2016; Kortatsi 2006) in wet season and groundwater recharge withdrawal in dry season is expected to induce redox activities/surge of pH and hence, the significant loading of pH in PC2. The influence of sea water intrusion (in-land site) is less probable due to insignificant loading of chloride.

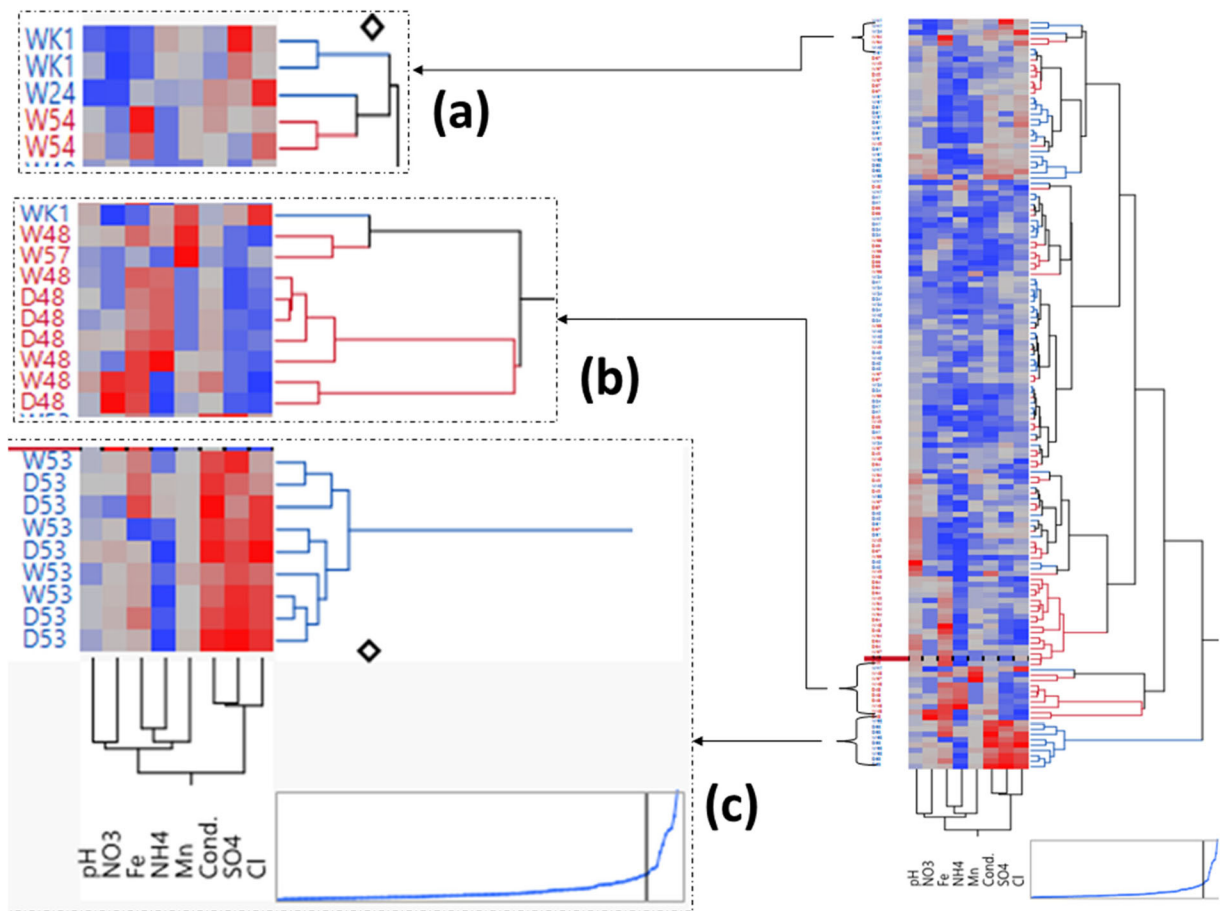
In the coastal site however, the PC separation in the bi-plot is high, accounting for 62.8% of the total variance as against 42.2% of the in-land site. However, the replication of PC1 significant parameters in the coastal plot and bi-plot of combined seasons suggest that coastal site parameters have stronger influence over that of the in-land site. Of importance is the significant positive loading of Mn and NH<sub>4</sub><sup>+</sup> alongside negative loading of NO<sub>3</sub><sup>-</sup> in PC2. This entails depreciative signal of nitrate and possible participation of Mn in autotrophic denitrification (Roy et al. 2017; Rysgaard et al. 2001).

As observed in the general variation, the hydrochemical signature of coastal sites points more to sampling well 53 (D53 & W53) majoring in both Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, conductivity, Fe and NO<sub>3</sub><sup>-</sup>. This mixed attribute of coastal (in the wet season) and in-land (in the dry

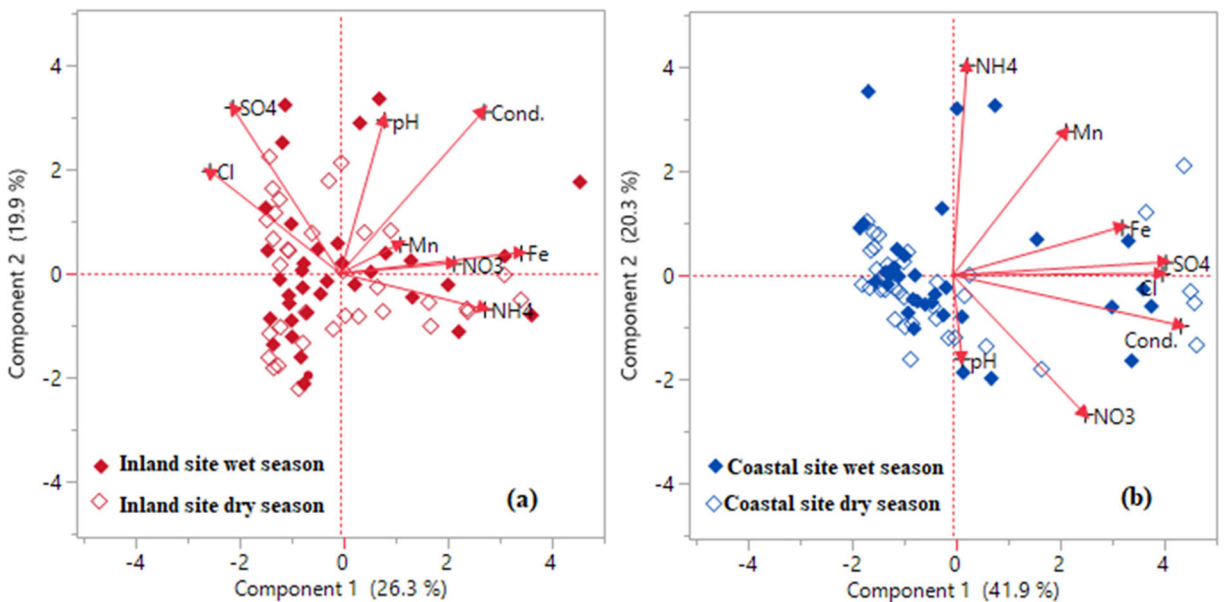


**Fig. 4** Canonical plot for the distribution of parameters across coastal plain and inland site





**Fig. 5** Two-way HCA dendrogram for the entire sample showing three major clusters **a** intersect cluster, **b** upstream inland-dominated cluster and **c** borderline coastal cluster



**Fig. 6** Bi-plot for the distribution of dry and wet season data in **a** in-land and **b** coastal sites

season) features is attributed to its borderline position, down gradient location and closeness of the sampling point to both river and industrial site. Ammonium loading in wet season of sampling well WK1 is attributed to debris of marine origin in the soil (Hedges and Oades 1997; Sweeney and Kaplan 1980) and heavy agricultural practice in the area. In in-land sampling site however, the loading of  $\text{NH}_4^+$ , Fe and  $\text{NO}_3^-$  dominates dry and wet seasons of sampling well 48, whereas sampling well W49 and W54 takes charge of  $\text{SO}_4^{2-}$  domination in wet season. It is suggested that the peculiar location of well 48 at the upgradient position expose it to distinguished state of low dilution influence from the river, and hence, it gives true representation of mineral and spatial influence in the area. The loading of chloride observed in dry season of sample D57 is attributed to recharge withdrawal and excessive evaporation (Han et al. 2015).

Finally, the fact that the plot is not distinct enough to demarcate the parameters on seasonal basis shows that the distinction of parameters on seasonal basis is not significant enough to be relied upon for explaining the behavioural pattern of the area.

#### *Hierarchical cluster analysis (HCA) – seasonal variation*

In reference to the reasons stated in “Principal component analysis” section, Fig. 7 shows how well sample D48 exhibits a unique feature that segregates it from the rest of the sampling points. The same projection can be applied to dry season sample D57, which tends to share its characteristic with samples close to the river (D49, D54 and D55) and those far away from it (D48). This behaviour may be explain by the groundwater flow around the area which was mapped-out by Islami et al. (2012) to be flowing from east to north west, heading towards Kelantan river. Hence, sampling well D48 is up gradient exhibiting unique characteristics, while D57 at the down gradient share its characteristics.

Sampling well D57 (the furthest away from water recharge) appeared only once at the upper constellation branch, indicating how the furthest samples away from water source differ in their properties based on the seasonal variation. Hence, the overlapping manifestation of results in sampling points between seasons is postulated to be justified by uniform hydrological condition, high precipitation and common geological formation of the area. This assumption is supported by PCA values of the most influential parameters in the

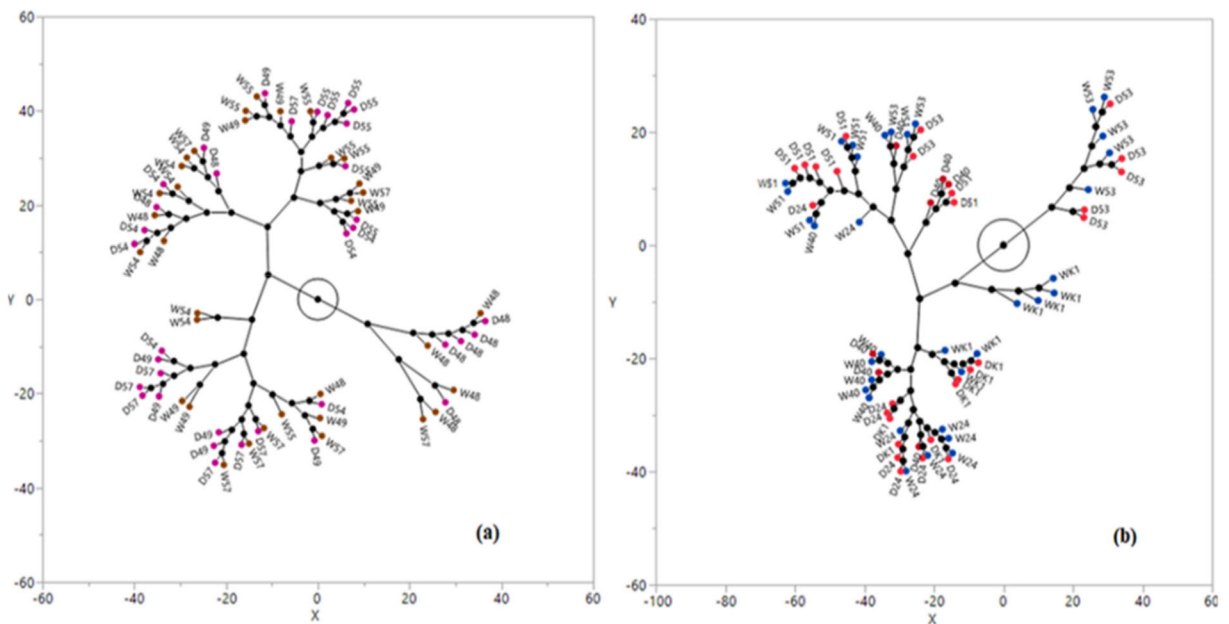
in-land site as abundant distributions of Fe reflect the common geological influence on the region.

In contrast to the in-land site, the right upper branch of the constellation plot in the coastal site (Fig. 7b) consists of wet and dry season of sampling well 53 (W53 & D53). It can be deduced from its proximity to the river and location within industrial zone that their effect overshadows the anticipated temporal variation (Mo et al. 2018). The grouping of WK1, D24 and D40 is corroborated by better PCA separation of the coastal site explaining up to 62.2% of the total variation.

#### *Discriminant analysis (DA) – seasonal variation*

As shown in Fig. 8, the conspicuous intersect of the two seasons in canonical plot justifies the narrow discriminant factors and explains why neither step backward nor forward analysis yield any significant factor of discrimination in coastal sites. In inland site, however, Mn is the only significant factor of discrimination. This may be as a result of the observed lower pH record of the dry season, which encourages dissolution of minerals in the soil (within the aquifer) to precipitate active Mn for Mn-induced denitrification (Chao 1972). The denitrification indicator is supported by high loading of Mn and Fe (Rysgaard et al. 2001) in the wet season of the in-land site than its corresponding dry season. This may be attributed to general dissolution of minerals caused by both rain wash down and general flooding in the area that has been reported to extend several kilometres away from the water source for a long period of time (Ismail and Haghroosta 2018). Also the sporadic occurrences of pyrite across the plain as reported by Enio et al. (2011) could be a contributing factor. The concentration of trace metals necessary for denitrification is minimal, reported to have the initial  $\text{Fe}^{2+}/\text{NO}_3^-$  molar ratio of 8. This can be explained by the proximity of standard oxidation potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  pair to that of the  $\text{NO}_3^-/\text{N}_2$  pair (0.75 V) (Zhu and Getting 2012). Hence, the average concentrations of both Fe (4.83 ppm) and Mn (0.26 ppm) in the water samples (alone) in this study are high enough to cause denitrification. Metals have different or complimentary role, as Fe is needed by cytochrome for electron transfers, and copper acts as a cofactor for both the nitrite and the  $\text{N}_2\text{O}$  reductases, whereas manganese is necessary for electron transfer and iron replacement (Vodyanitskii and Mineev 2015).

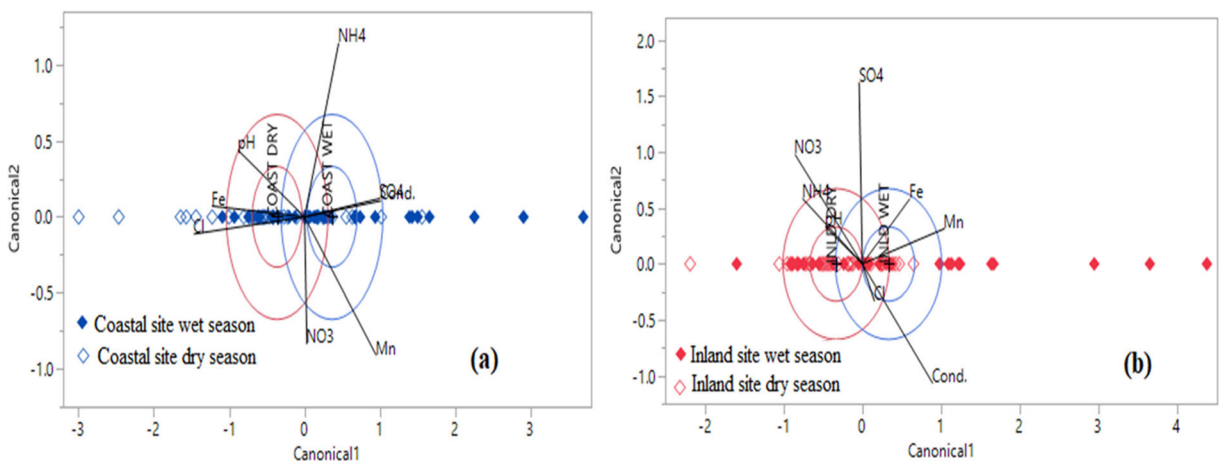
The discriminant analysis of the in-land sites supports PC distribution of the site. However, in contrast to



**Fig. 7** Constellation plot of dry and wet season for **a** In-land sampling sites and **b** coastal sampling sites

in-land sampling sites, the coastal samples reveal less loading and more centralised classification of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  tilting towards the wet season. The less loading is a manifestation of reduced significance of a parameter in relation to other parameters and in this case is an indication of faster chemical reduction. This may be attributed to high redox activity on the coastal site during the wet season, wherein the rain water or water from flood dissolves labile minerals (readily oxidisable or reducible mineral deposits on the coastal lines) and renders reducing or oxidising agents more active. In addition,

agricultural practice of rice and tobacco plantation that ensures heavy application of urea and animal dung fertilisers could be a contributing factor. Another factor is that of the dissolution due to flooding, being a common occurrence in the area. As such, combinations of active redox condition and constant supplies of reducing agents are envisaged to be responsible for this intermediary distribution between  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Hence, the extent of overlap of wet season distribution into the dry season qualified  $\text{NO}_3^-$  in PC1 of wet season. It is therefore deduced that lack of uniform distribution of



**Fig. 8** Canonical plot for seasonal variation **a** wet and dry season for coastal sampling sites and **b** wet and dry season for inland sampling sites

labile minerals on the in-land site could be responsible for the differential response of nitrate remediation between the in-land and coastal site.

### Spatial-based variation

The pairing pattern of data in spatial-based variation ensures that any observed variation is caused by the hydrogeological characteristic of the site or anthropogenic influence. Formed by pairing data of different site (coastal plain site and inland site) obtained from the same season (either wet or dry season), the following are obtained.

### Principle component analysis (PCA) – spatial

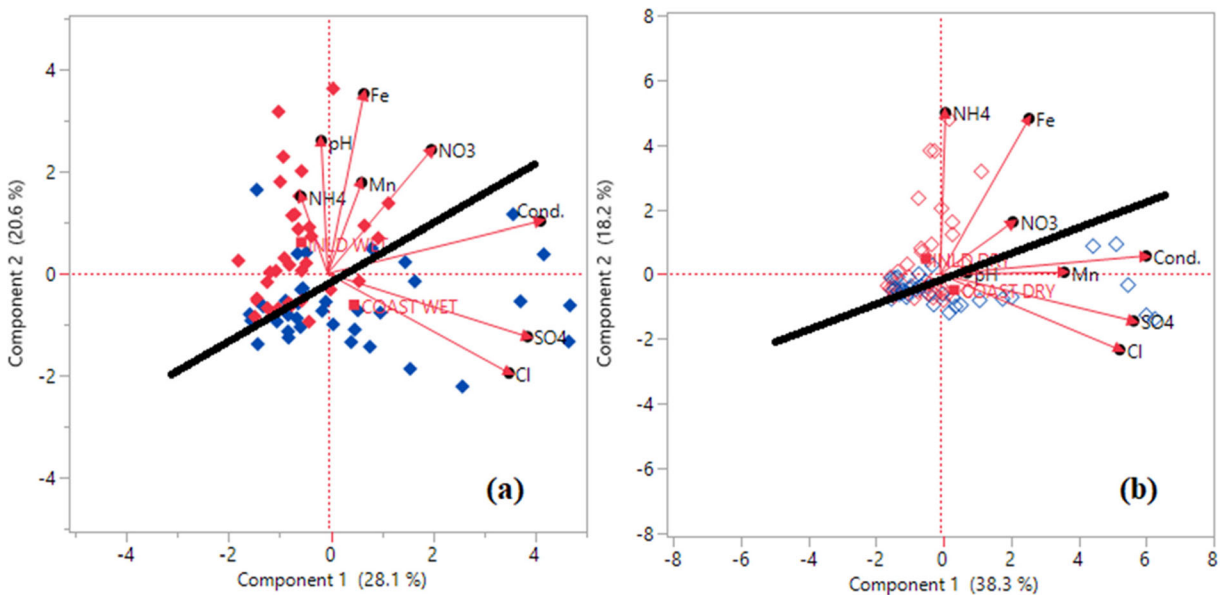
Figure 9 shows the bi-plot of in-land and coastal sites in wet and dry seasons. The separation of the distribution based on the location is so distinct that a sharp dividing line is drawn between the locations in both seasons. PC's extracted with Eigen values > 1 explained up to 48.7% and 56.4% of the total variance in wet and dry seasons, respectively.

The analysis of the hydrochemical characterization of the two spatial variations in wet season shed light on three influential factors for predicting behaviours of groundwater in the area. These factors are direction of the groundwater flow, soil composition (mineral content) and water recharge source. Considering the bearing

of the groundwater flow, it is logical to observe that upstream sampling point 48 is only loaded with one of the most abundant mineral resources in the area which is Fe.

In the same vein, both the downstream sampling points 54 and 53 measure in conductivity loading with sampling well 53 having dominance in  $\text{SO}_4^{2-}$  (being at the proximity to both river, build area and industries), while sampling well 54 is loaded with  $\text{NH}_4^+$  and Mn (speaking volume of its strategic downstream location and proximity to farming sites). Sampling well 55 that share less loading of  $\text{NO}_3^-$  with wells WK1 and W24 is attributed to recharge and dilution influence of the river that align with the groundwater flow.

It is pertinent to observe that the domineering influence of sea-associated parameters (conductivity, chloride and sulphate) prevails in PC1 whenever a coastal sampling is involved. It can also be deduced from the dry season that, with the influence of fertilisers in a less diluted condition, the precedence of  $\text{NH}_4^+$  significance (in PC 2) over that of  $\text{NO}_3^-$  (in PC4) is an indication of delayed conversion process. In wet season however,  $\text{NO}_3^-$  fluctuation manifests in PC2 and PC3 (with negative sign), while  $\text{NH}_4^+$  is loaded in PC3. This suggests prompt conversion and denitrification process as the condition is more favourable in wet season. Generally, in wet season, dissolution process and high temperate climate facilitate microbial activity. However, the coastal site has a peculiar and favourable attributes of



**Fig. 9** Bi-plot for distribution of data in both coastal and inland sites during **a** wet season and **b** dry season

harbouring both labile mineral- and organic-rich soil, which are so active in oxidation-reduction process.

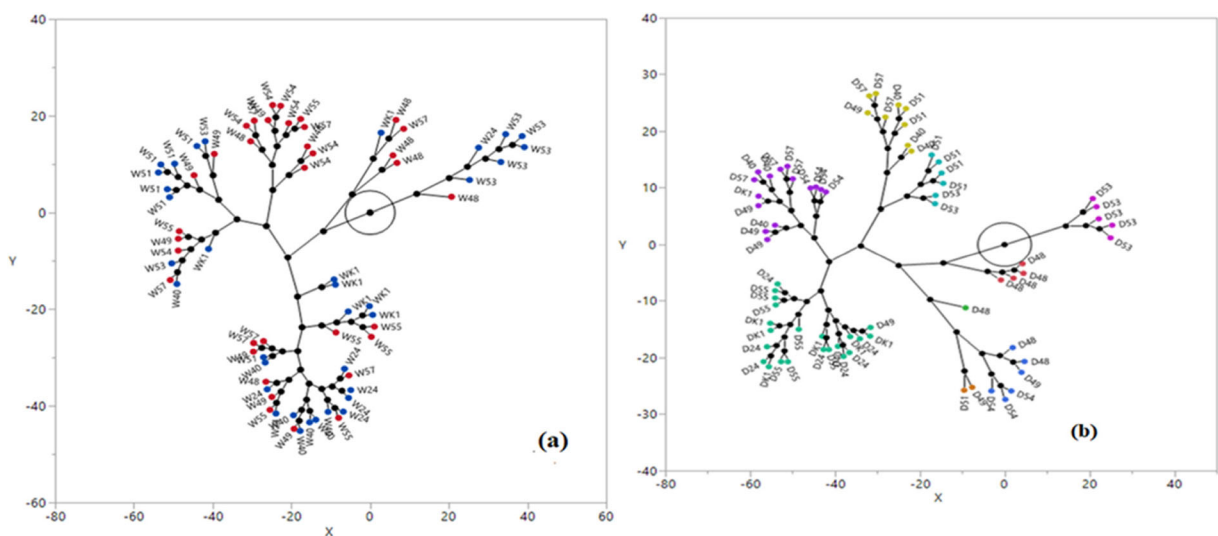
*Hierarchical cluster analysis (HCA) – spatial*

The right-hand branch of Fig. 10 a consists of down-gradient coastal sampling sites of W53 interspersed with up-gradient sample W48, W57 and WKI. As explained by the hydrological signature of the site, well 53 share high loading of conductivity and  $SO_4^{2-}$  with well 48. The commonality amongst the two is proposed to be connected with the pattern of groundwater flow and similar agricultural activities in both locations. Hence, spatial influence could be the unifying factor for this grouping.

Lower branch is riddled with coastal-based sampling site (having few in-land sampling sites), while the right-hand side of the upper left canonical branch is dominated with in-land sampling sites. Within the branch of the latter, more of the coastal sampling wells W53, W51 and W40, which are closer to the in-land sampling sites than the coastal plain, are present. This, as suggested by Roslan et al. (2010), indicates the strength of the hypothesis of proximity influence of the sea to the sampling site. The constellation plot of the dry season in coastal and in-land sites (Fig. 10b) indicates a sheer similarity in behaviour between sample D53 of the coastal site and sample D48 of the in-land site. This may be attributed to groundwater flow pattern and proximity to rivers.

*Discriminant analysis (DA) – Spatial*

In contrast to season-based (temporal) discriminant analysis, the spatial DA differs in majoring on Fe, Mn,  $NO_3^-$  and conductivity for coastal dry season, coastal wet season, in-land dry season and inland wet season samples, respectively. The relative apportionment of  $NO_3^-$  and conductivity on the inland site shows less attenuation capacity of the nitrogen-based compound in the site. The influence of dilution factor (brought about by temporal changes such as excessive precipitation or flood), soil nature and geological formation of the coastal sites, tends to support natural attenuation of  $NO_3^-$  more than that on the in-land site. The combination of these factors in coastal sites makes it distinct and more susceptible to denitrification than in-land sites because the soil at the coastal sites was once covered by the sea before the Holocene. This as attested by previous researchers has a special type of Fe that can only be deposited by inundation from the sea webs. More so, the differential manifestation of Fe in dry season and Mn in wet season of the coastal site supports the presence of pyrite formed by sea water inundation (Enio et al. 2011; Roslan et al. 2010) and dissolution influence of wet season. This indicates ubiquitous distribution of Fe around the area as it is still significant even without much dissolution process (in dry season). This uniform distribution may not be found in the inland site as the Fe is though high, often heterogeneously dispersed. The Mn however, seems to be significant only after dissolution in wet season, which may be due to rain or flooding.



**Fig. 10** Spatial constellation plot for **a** wet season of coastal and inland and **b** dry season of coastal and inland sites



This suggests its sparse distribution across the area. In contrast with the inland site,  $\text{NO}_3^-$  and conductivity were found to be the most significant parameters, suggesting that the influence of anthropogenic activities, consisting of irrigation, which tends to apply more of nitrate-based fertilisers, and domestic wastes (industrial complexes) are the possible determinant factors at the inland sites.

The step forward analysis of the wet season canonical plot revealed parameters in the order of reducing significance from  $\text{Cl}^-$ , Fe to  $\text{SO}_4^{2-}$ , whereas that of the dry season gave  $\text{Cl}^-$  and Fe, respectively. This signifies that the dominant active specie in wet season is a combination of sea influence and dissolution of mineral substances in the soil. More so, the sampling locations within which these parameters are loaded suggest that the impact of human activities around the sampling points add to the account of making  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  significant. In dry season however, recharge withdrawal and significant evaporation concentrate residual species (Kortatsi 2006) thereby making them more prominent.

In summary, the application of the principal component analysis, followed by cluster analysis, which utilises the factor scores obtained from the PCA and categorises the variables into similar clusters is a useful tool in characterising interrelated and complex variables like hydro-geochemical data. As it can be seen from the results obtained, the grouping is validated using discriminant analysis. For confirmatory purposes, the HCA clusters tallies with the PCA's most significant variables (PC 1 and PC2). The results obtained in discriminant analysis however tends to discriminate the variables on the basis of their seasonal-based discrimination or location based of the sampling sites. As such, hydro-geochemical characterisation based on the temporal and spatial analysis is deduced from the results (Zhang et al. 2009).

#### Vertical distribution of denitrification parameters in Bachok soil

Figure 11 Demonstrates the plot for the distribution of denitrification-relevant parameters across the eight soil layers (from P1 to > 1 m) taken. While nitrate, sulphate and TOC values are high on the top soil (P1), the concentration of Fe and Mn are relatively low (Table 2). This is well expected due to agricultural practice in the area, which ensures fertiliser application (Kaown et al. 2009) and humus found on topsoil (Azlan

et al. 2012; Haynes and Naidu 1998; Roslan et al. 2010; Zanella et al. 2011)

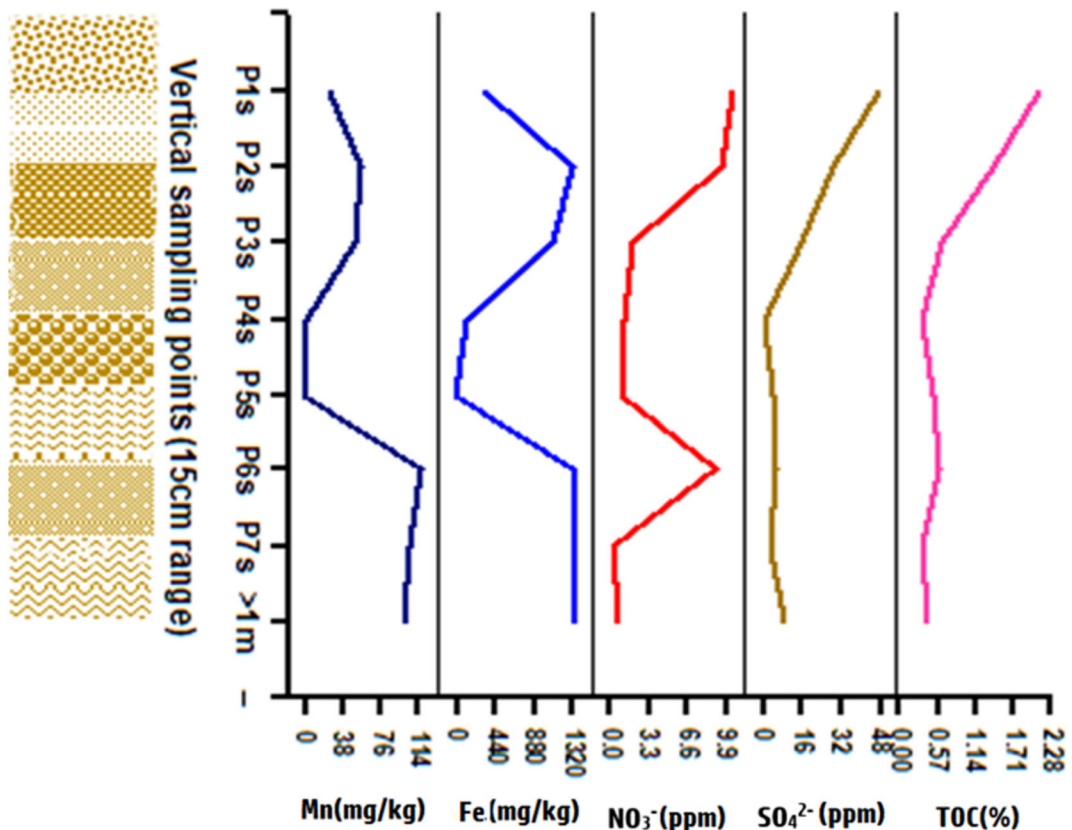
As the concentration of Fe begins to rise, the nitrate concentration declines with both dropping to the lowest level within layers 3–4. The attenuation of Fe across the layers here is attributed to the mineral distribution in the crust within the soil rather than reductive process in denitrification. This is because if autotrophic denitrification were taken place, the concentration of Fe would remain high (Rysgaard et al. 2001). More so, the top soil is rich in oxygen, which is preferentially utilised over anaerobic electron acceptors like Fe (Scherer et al. 2000).

This is because if autotrophic denitrification were taken place, the concentration of Fe would remain high (Rysgaard et al. 2001). More so, the topsoil is rich in oxygen, which is preferentially utilised over anaerobic electron acceptors like Fe (Scherer et al. 2000). The nitrogen transformation process from  $\text{NO}_3^-$  to either  $\text{NO}_2^-$ ,  $\text{N}_2$  or  $\text{NH}_4^+$ —through denitrification, fixation ammonification and nitrification—is another factor of consideration (Westermann and Ahring 1987). However, both  $\text{NO}_3^-$  and Fe shoot up at layers 5–6, only for  $\text{NO}_3^-$  to decline from layer seven onwards, leaving the Fe concentration high. This suggests autotrophic denitrification activity especially that the TOC value is low at the point.

Since contaminant reduction at the iron surface stimulates microbial growth and reductive biotransformations through the production of water-derived  $\text{H}_2$  (Da Silva et al. 2007), it is hypothesised that the more closer the pollutants are to the vadose zone, the more likely it is that denitrification will occur (Groffman and Tiedje 1989). It is therefore possible to draw a connection between the analysis of the soil and that of the groundwater. The attenuation pattern of nitrate across the soil strata down to the water table explain how the parameters ends up being what they are in groundwater.

Two possible scenarios are deduced from the pattern of the above result.

1. A combination of heterotrophic denitrification (to a lesser extent) and  $\text{NO}_3^-$  interconversion to ammonium from P2–P5, causing the sharp decline of  $\text{NO}_3^-$  concentration within the layers. The attenuation pattern of sulphate declines with that of TOC is similar (Fig. 10), suggesting a possible indication of its competition with  $\text{NO}_3^-$  for degrading the organic



**Fig. 11** Vertical distribution of key players in denitrification across the soil layers

matter (Canfield et al. 1993) and hence, paving way for possible conversion of  $\text{NO}_3^-$  to other forms of nitrogen (Westermann and Ahring 1987). This suggestion is supported by reported competition of oxygen-bearing specie with nitrate in denitrification (Wang et al. 2018). The possible occurrence of heterotrophic denitrification is attributed to presence of long-aged marine deposition at coastal

plains, in the form of detritus (Biddanda and Pomeroy 1988).

- Autotrophic denitrification from P6 and above because of sharp drop of  $\text{NO}_3^-$  concentration sustained high concentration of Fe and Mn and low level of TOC. The re-emergence of  $\text{NO}_3^-$  at P5 is attributed to nitrification within the medium as nitrate is more stable amongst the nitrogen species

**Table 2** Distribution of parameters in soil layers

Sampling point	Mn (mg/kg)	Fe (mg/kg)	$\text{NO}_3^-$ (ppm)	$\text{SO}_4$ (ppm)	TOC (%)
P1s	25.77 ± 0.32	319.33 ± 4.04	10.55 ± 0.10	47.99 ± 0.12	2.12 ± 0.02
P2s	57.40 ± 0.84	1332.67 ± 10.21	9.63 ± 0.56	29.37 ± 0.03	1.47 ± 0.06
P3s	51.60 ± 0.82	1129.00 ± 5.57	2.04 ± 0.06	16.74 ± 0.06	0.69 ± 0.06
P4s	2.57 ± 0.25	146.68 ± 7.51	1.31 ± 0.02	1.19 ± 0.01	0.36 ± 0.01
P5s	0.10 ± 0.07	13.66 ± 0.23	1.19 ± 0.02	4.87 ± 0.02	0.52 ± 0.01
P6s	119.40 ± 2.25	1332.27 ± 2.27	9.22 ± 0.04	5.67 ± 0.02	0.62 ± 0.01
P7s	105.57 ± 0.65	1350.60 ± 4.80	0.42 ± 0.04	3.47 ± 0.04	0.37 ± 0.02
> 1 m	100.67 ± 0.81	1360.50 ± 3.46	0.94 ± 0.06	9.09 ± 0.09	0.47 ± 0.04

(Kurtén et al. 2008; Sebranek and Bacus 2007; Siu and Henshall 1998)

It is logical to assume that from P1–P5, the geochemical condition is not favourable to the facultative microorganism for anaerobic reduction and hence their activity is witness at P6 and above. The sampling layers (P6 and above) have high moisture, which encourages Fe corrosion for hydrogenotrophic denitrification (autotrophic). This prediction is supported by the average ORP values of 485 measured (in this study) for the three wells, providing favourable condition for the microbes (Suslow 2004). More so, nitrate serves as a nutrient for biostimulation of native microflora (Ye et al. 2017). So, a natural combination of heterotrophic denitrification (through the utilisation of organic detritus) and autotrophic denitrification (through the anaerobic corrosion of Fe-bearing mineral in the soil) is hereby deduced to have occurred.

Finally, the connection between the analysis of soil samples and water samples analysis is seen in the trends of nitrate attenuation from the surface of the soil across the strata, down to the water level. The distribution of parameters across the strata explains how the parameters end up being what they are in groundwater. Though, the readily soluble parameters, which may not be found on topsoil may differ in concentration from soil to groundwater significantly, their distribution indicates a continuity of attenuation process from top of the soil to water table.

## Conclusion

This study measures the physiochemical parameters of groundwater samples taken from established low-nitrate agricultural site of Bachok to investigate the hydrogeochemical factors responsible for high denitrification in the area. Using three different chemometric tools, the findings reveal that spatially induced variation is more influential than temporal-based variation. Five major parameters are extracted to be the determining factors with three (conductivity,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) assigned to coastal sites and two ( $\text{Fe}$ ,  $\text{NO}_3^- / \text{NH}_4^+$ ) assigned to in-land sites. The result of soil analysis suggests multiple reduction process that is dependent on depth and matrix composition (long-aged marine deposition and sea-associated Fe containing mineral). This study further illustrates that the area is characterised with active

engagement of nitrogen cycle activities. Constant flood in the area is also sought to be influential in dictating the hydrogeochemical characteristic of the area. Hence, the high-denitrification potential in the coastal site is attributed to presence of highly redox condition and occurrence of both heterotrophic and autotrophic denitrification. It is recommended that further research be conducted to see to the possibility of utilising the soil as impregnating agent for in situ denitrification process especially in sites with low denitrification. Finally, the study highlights a useful perspective of assessing the temporal and spatial distribution of data across sites with the view of exploring the influence of labile portion of natural resources for broader application. This is because though, Fe is present in both coastal and inland region, the special combination of sea inundated Fe with organic marine deposit at the coastal plain seems to play greater role in denitrification potential of the coastal plain.

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