


Evaluating Groundwater Quality Using Multivariate Statistical Analysis and Groundwater Quality Index

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Abstract

Under pressure from surface water pollution and climate change, groundwater becomes a critical water source. Information on groundwater quality could contribute to effective groundwater management. This study was carried out to utilize multivariate statistical analysis and the groundwater quality index (GWQI) to evaluate groundwater quality in Ca Mau Province, Vietnam. Twenty-five groundwater samples from residential-urban areas, cemetery areas, landfill areas, and saline intrusion areas were collected for this study. Groundwater quality was evaluated using the National Technical Regulation on Groundwater Quality (QCVN 09-MT:2015/BTNMT) and GWQI. Principal component analysis (PCA) was used to identify potential polluting sources and key variables influencing groundwater quality. Cluster analysis (CA) was applied to cluster groundwater quality, and the sites were recommended for future monitoring. The results revealed that $\text{NH}_4^+\text{-N}$ contaminated groundwater in the landfill area, while the saline intrusion area was polluted by TDS and $\text{NH}_4^+\text{-N}$. The groundwater quality classified as excellent, good, poor, and very poor accounted for 44, 40%, 12%, and 4%, respectively. Cluster analysis divided groundwater quality into four groups, mainly based on the presence of $\text{NH}_4^+\text{-N}$ and TDS. Nine groundwater sampling locations could be removed from the current groundwater quality program but still ensuring representativeness as a result of CA. PCA proposed two main sources of variation in groundwater quality at each residential-urban area: the cemetery area, the landfilling area, and the saline intrusion area. The groundwater parameters (i.e., pH, TDS, permanganate index, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Fe) should be continued to monitor. Domestic and industrial wastewater discharge, leachate from cemeteries and landfills, the nature of groundwater aquifers, and seawater intrusion could be potential sources of groundwater variation. The current findings provide scientific information for local environmental authorities to manage and monitor groundwater quality in the study area.

Keywords: Ammonium; Ca Mau Peninsula; Groundwater Quality Index (GWQI); Multivariate Analysis.

1. Introduction

Surface water pollution, climate change-induced drought, and sea level rise lead to groundwater become more important for human beings and ecosystems [1–5]. Groundwater has been used for various purposes, such as domesticity, irrigation, transportation, and industry [6–9]. The benefit of groundwater use to ecosystems and human beings is very huge [10, 11]. However, groundwater quality has been influenced by both natural and anthropogenic activities [8, 9, 12]. The natural processes influencing groundwater quality include groundwater recharge, rock-water interactions, mineral weathering, and contaminated water from the adjoining aquifer [8, 9, 13]. Anthropogenic activities include improper groundwater exploitation, intensive applications of agrochemicals, industrial production,

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waste and wastewater discharge, and urbanization [8, 12, 14]. Former studies presented that groundwater quality is polluted. For instance, Giao and Nhien (2023) [15] reported that groundwater quality in the Vietnamese Mekong Delta has been polluted by heavy metals and coliforms, and the causes of pollution may be from improper treatment of waste in domestic activities, agricultural and industrial production. The study by Laonamsai et al. (2023) [8] also found that Zn, Hg, Pd, Fe, and Mn contaminated groundwater quality in Thailand. The potential sources of groundwater pollution in Thailand were identified as untreated sewage discharge and fertilizer usage, in addition to the characteristics of geological formations. The other study found that groundwater was contaminated by iron, manganese, aluminium, and organic matter, and the significant origins of contaminants are from agriculture (the use of fertilizers and pesticides), urban waste, and industry [12]. Consumption of contaminated groundwater may pose many risks to human health, such as diarrhea, vomiting, shortness of breath, splenic hemorrhage, blue baby syndrome, or methemoglobinemia [16, 17].

Groundwater quality monitoring plays a crucial role in pollution prevention. The monitoring data (including sampling sites, parameters, and frequencies) could provide useful information for the identification of sources of groundwater variations. This information is required for the planning of groundwater usage. One of the basic ways to evaluate the characteristics of groundwater quality is to compare individual measured concentrations of groundwater parameters to corresponding values regulated by national or international standards [15, 18]. For the overall groundwater quality that is presented for a well or an aquifer, the groundwater quality index (GWQI) is used. GWQI calculation requires the use of a set of preidentified groundwater quality data, so the groundwater quality between space and time is easily compared and ranked [8, 9, 15, 19]. GWQI has been widely applied in several former studies [3, 8, 9, 12, 13, 15]. Recently, multivariate statistical methods, including principal component analysis (PCA) and cluster analysis (CA), have also been widely applied in studying groundwater quality [3, 18, 19]. PCA is used to reduce data size, providing information on potential polluting sources and key variables influencing groundwater quality [3, 20]. CA is utilized to cluster groundwater quality parameters into various groups based on the similarities or dissimilarities between space and time of the identified groundwater quality variables [3, 13, 15, 18]. PCA and CA could be used simultaneously to recommend the site, the parameters, and the frequencies of environmental quality monitoring, including groundwater.

Ca Mau Peninsula, a coastal province, is one of the five major regions of the Mekong Delta of Vietnam (1.6 million hectares, accounting for 43% of the total area of the Mekong Delta), playing an important role in the economic and social development of the region. With rapid social and economic growth, the demand for water use significantly increases. However, surface water in Ca Mau has been seriously polluted by waste discharge from industrial zones, aquaculture, agricultural, residential, and landfills [21, 22]. Therefore, groundwater has been becoming more important for water sources for the production and daily activities in Ca Mau province. Several studies have been carried out to evaluate groundwater quality in the Vietnamese Mekong Delta [15, 18, 23, 24]; however, information on groundwater quality in Ca Mau is limited. This study is conducted to evaluate groundwater quality in Ca Mau province using national technical regulations on groundwater quality and the groundwater quality index (GWQI). In addition, CA and PCA were also utilized to cluster groundwater quality and identify potential polluting sources affecting groundwater quality in the study area. The findings of the current study could contribute to groundwater quality monitoring and pollution prevention. The structure of this article comprises of the abstract, introduction, materials and methods, results and discussion, conclusion, and references.

2. Research Methodology

2.1. Description of the Study Areas

Ca Mau Peninsula is the southernmost land in the Mekong Delta region, with an area of about 1.6 million hectares, surrounded by the East and West seas. The region has an interlaced and interwoven system of rivers and canals, accounting for about 3.02% of the natural area, in which there are many large rivers with deep water levels, leading to alluvial deposits inland such as the Cua Lon River, Ganh Hao, Bay Hap, Song Doc, and Cai Tau [25]. With an average elevation of 0.5–1.5 m above sea level and a 254 km-long coastal area, there are three sides of the East, South, and Southwest, which are influenced by two tidal regimes of the West Sea (irregular tides) and the sea. In the winter, Ca Mau is considered to be the most severely affected area by saline intrusion. Along with the process of socio-economic development, the surface water of the region has been significantly polluted since groundwater sources have become an important source of clean water for daily life and industrial activities. According to the survey results of the Vietnam Geological Map Federation, the area's groundwater has relatively large reserves. The potential exploitation reserve of groundwater on the Ca Mau Peninsula is about 11,456,479 m³ per day. In addition, according to the statistics of the whole Ca Mau Peninsula, the area that can be exploited for pale groundwater is 13,901.9 km² (accounting for 83.4%), and the area of saline aquifers is 2,758.1 km² (accounting for 15.6%). According to hydrogeological characteristics of the area, there are all 7 aquifers, including Holocene aquifer (qh), Upper Pleistocene (qp₃), Upper Middle Pleistocene (qp₂₋₃), Lower Pleistocene (qp₁), Middle Pliocene (n₂²), Lower Pliocene (n₂¹), and Upper Miocene (n₁³) [25].

2.2. Description of Groundwater Sampling and Analysis

Groundwater quality data were collected from the Department of Environment and Natural Resources, Ca Mau Province, Vietnam. Twenty-five groundwater samples (GW1-GW25) were collected at 9 districts, with a frequency of monitoring 3 times per year (June, September, and December) in 2022. The monitoring period for the first phase was from June 21 to 24, 2022. Four areas are subjected to groundwater sampling, including residential-urban areas (GW1-GW8), cemetery areas (GW9-GW17), landfills (GW18-GW22), and areas affected by saline intrusion (GW23-GW24). Groundwater samples were collected and stored in PE plastic bottles, refrigerated or preserved with chemicals to be transported to the laboratory as soon as possible, ensuring the method of sampling and preserving samples according to TCVN 6663-1:2011, TCVN 6663-3:2016, and TCVN 6663-11:2011. The locations of groundwater samples are detailed in Figure 1 and Table 1. Six physical and chemical parameters of groundwater, including pH, total dissolved solids (TDS), permanganate index (PI), ammonium ($\text{NH}_4^+\text{-N}$), nitrate ($\text{NO}_3^-\text{-N}$), and iron (Fe), were examined. The pH parameters were measured directly in the field according to TCVN 6492:2011 (ISO 10523:2008) and SMEMW 4500.B:2012. The parameters comprising TDS, permanganate index, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Fe were analyzed in the laboratory according to standard methods [26]. Specifically, the TDS was determined by the drying method at 180°C according to the SMEWW 2540.C:2012 standard. The permanganate index is determined according to TCVN 6186:1996 (ISO 8467:1993 (E)). Determination of $\text{NH}_4^+\text{-N}$ concentration by manual spectrometric method according to TCVN 6179-1:1996 (ISO 7150-1:1984E). $\text{NO}_3^-\text{-N}$ was determined by the spectrophotometric method using 2,6-dimethylphenol (TCVN 7323-1:2004, ISO 7890-1:1986). Determination of iron by spectrometric method using 1,10-phenanthroline reagent (TCVN 6177:1996, ISO 6332:1988). The analysis of groundwater samples was carried out by the Southern Environment and Natural Resources One Member Limited Liability Company.

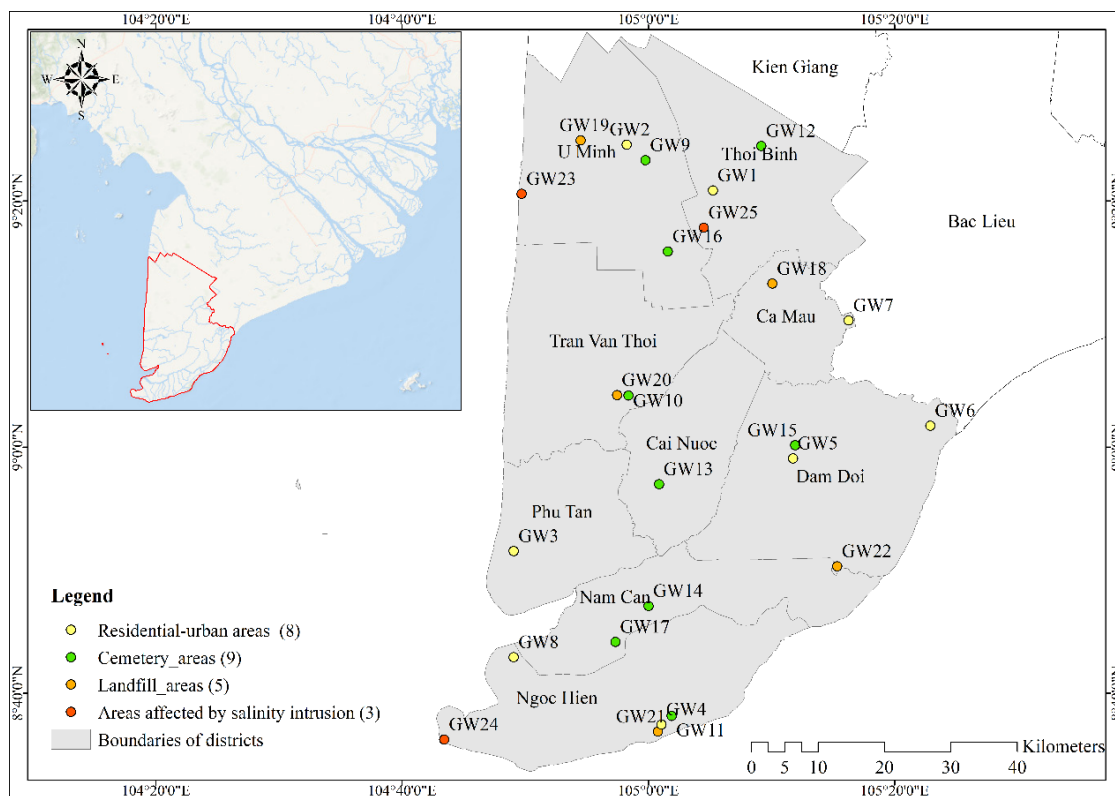


Figure 1. Map of the sampling locations in the study area

Table 1. Brief description of the sampling locations

Areas	Code	Location
Residential and urban	GW1	Area 4, Thoi Binh town, Thoi Binh district
	GW2	Area 2, U Minh town, U Minh district
	GW3	Area 7, Cai Doi Vam town, Phu Tan district
	GW4	Area 1, Thi Trac Rach Goc, Ngoc Hien District
	GW5	Dam Doi town, Dam Doi district
	GW6	Ganh Hao estuary area, Tan Thuan commune, Dam Doi district
	GW7	Tac Van Market, Tac Van Commune, Ca Mau City
	GW8	Residential Area 1, Cai Doi Vam Town, Phu Tan District

Cemetery	GW9	Cemetery area in Hamlet 1, Nguyen Phich Commune, U Minh District
	GW10	Cemetery area of Tran Van Thoi district
	GW11	Cemetery area cluster 6, TT. Rach Goc, Ngoc Hien district
	GW12	Nha Dao - the land of the Holy Family of Huyen Su in Hamlet 3, Tri Phai Commune, Thoi Binh District
	GW13	Cemetery area of Cai Nuoc district
	GW14	Cemetery area of Nam Can district
	GW15	Area near Dam Doi district cemetery
	GW16	The area of people's cemetery in Tan Phu hamlet, Khanh An commune, U Minh district
	GW17	Area of Truong Duc cemetery, Lam Hai commune, Nam Can district
Landfill	GW18	The concentrated landfill area of Ca Mau province, Tan Xuyen ward, City. Ca Mau
	GW19	The area of the cluster landfill site 2. U Minh town, U Minh district
	GW20	The landfill area of cluster 5, Tran Van Thoi town, Tran Van Thoi district
	GW21	The landfill area of cluster 1, Rach Goc town, Ngoc Hien district
	GW22	Landfill area in Hai An hamlet, Nguyen Huan commune, Dam Doi district
Areas affected by salinity intrusion	GW23	Hamlet 3, Khanh Hoi Commune, U Minh District
	GW24	Mui Hamlet, Dat Mui Commune, Ngoc Hien District
	GW25	Hamlet 2, Hang Vinh commune, Nam Can district

2.3. Data Analysis

The difference in groundwater quality parameters (pH, TDS, permanganate index, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Fe) at various subject areas was examined using one-way analysis of variance (One-way ANOVA), followed by Duncan's test at a significant level of 5% ($p < 0.05$) using SPSS software version 20.0. The groundwater quality was evaluated by comparing the measured data to the one that is being regulated in the National Technical Regulation on Groundwater Quality (QCVN 09-MT:2015/BTNMT) [27]. The limit values of groundwater parameters according to QCVN 09-MT:2015/BTNMT are detailed in Table 2.

Table 2. Limit values of the used groundwater parameters in this study

No.	Groundwater parameters	Limit values
1	pH	5.5-8.5
2	TDS	1500
3	Permanganate index	4
4	$\text{NH}_4^+\text{-N}$	1
5	$\text{NO}_3^-\text{-N}$	15
6	Fe	5

Overall groundwater quality in the study area was assessed using groundwater quality index (GWQI). GWQI was calculated using Equation 1. In this study, the GWQI index was calculated from six parameters, including pH, TDS, permanganate index, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and F.






$$\text{GWQI} = \sum_{i=1}^n \left[\left(\frac{W_i}{\sum_{i=1}^n W_i} \right) \times \left(\frac{C_i}{S_i} \times 100 \right) \right] \quad (1)$$

where: C_i is the concentration of each parameter, S_i is the limit value of each parameter specified in QCVN 09-MT:2015/BTNMT, W_i is the weight of each parameter calculated by Equation 2.

$$W_i = \frac{\frac{1}{\sum_{i=1}^n \left(\frac{1}{S_i} \right)}}{S_i} \quad (2)$$

GWQI classifies groundwater quality into five levels, which are presented in Table 3.

Table 3. Classification of groundwater quality based on GWQI

No.	Values	Groundwater quality	Colour
1	$\text{GWQI} < 50$	Excellent	
2	$50 < \text{GWQI} < 100$	Good	
3	$100 < \text{GWQI} < 200$	Poor	
4	$200 < \text{GWQI} < 300$	Very poor	
5	$\text{GWQI} > 300$	Unsuitable for drinking	

In this study, principal component analysis (PCA) was used to analyze 6 observed chemical and physical variables related to groundwater quality in Ca Mau. PCA is one of the widely used multivariate statistical techniques in environmental quality assessment and description. This method allows us to reduce the initial large data set into exploratory principal components (PCs) containing the most critical parameters affecting environmental quality [3]. When analyzing PCA, the number of PCs retained to explain the change in groundwater quality is mainly based on Eigenvalues, and the larger the PC value, the greater the contribution to the change in environmental quality and a collection of the main pollution sources for water bodies. Usually, principal components with Eigenvalues greater than 1 will be retained for evaluation [3, 28, 29]. The main components in this study were determined by varimax rotation. When choosing environmental variables correlated with each PC, the factor load is divided into 3 levels: (1) strong when > 0.75 ; (2) medium when fluctuating in the range of $0.75-0.5$; and (3) weak when fluctuating in the range of $0.5-0.3$ [3]. Cluster analysis (CA) is one of the multivariate statistical methods that group monitoring objects based on their attributes [29]. In this study, CA is applied to assess the level of groundwater pollution and group monitoring sites with the same physio-chemical characteristics in one group and different physio-chemical characteristics in different groups. Cluster analysis was performed on normalized data using the Ward method, and Euclidean distance was used to measure the similarity between groundwater quality variables [14, 29]. The resulting clusters of CA are presented in the form of dendrograms, clearly reflecting the level of water pollution and the similarity between monitoring locations. PCA and CA in this study were performed using PRIMER software version 5.2.

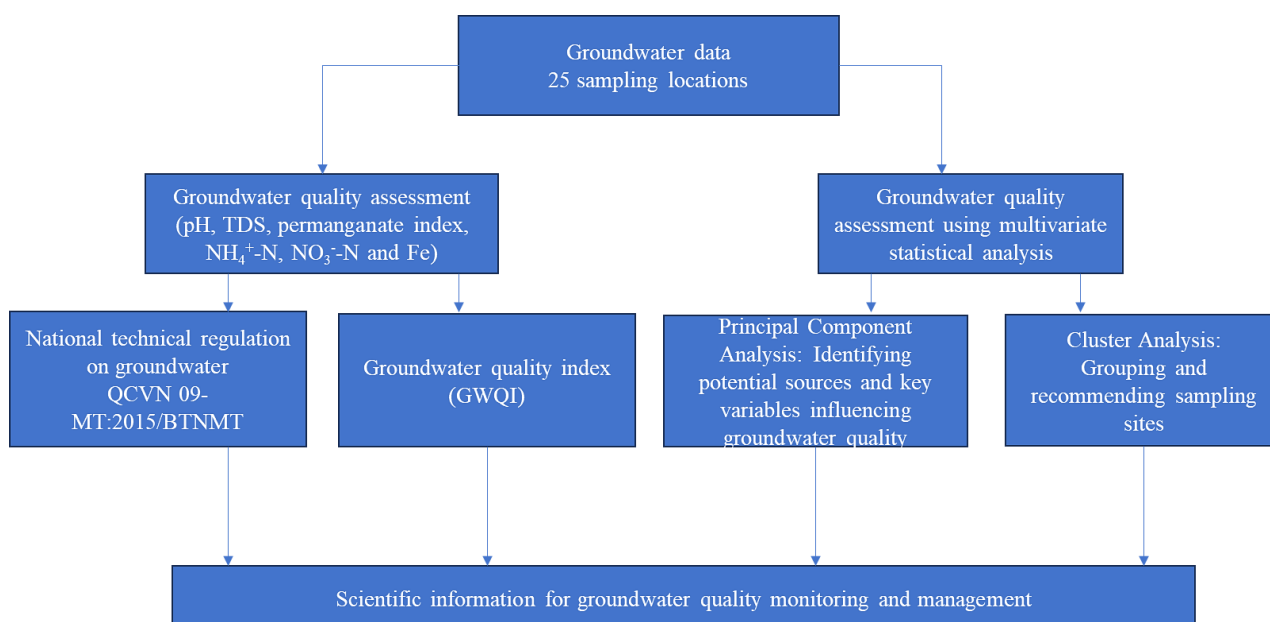


Figure 2. Flow chart of the study

3. Results and Discussion

3.1. Physical and Chemical Characteristics of Groundwater in the Ca Mau Peninsula

pH is one of the important water quality parameters that determines the alkalinity or acidity of groundwater [30]. The results showed that the average pH value in groundwater at four impact areas fluctuated in the range of 7.64 ± 0.45 – 8.04 ± 0.36 , reaching an average of 7.81 ± 0.46 . As can be seen, the groundwater in the study area was slightly alkaline (Figure 3). pH in groundwater at the landfill area was the lowest and had a statistically significant difference ($p < 0.05$) with that at the cemetery area. Low pH in groundwater at landfill sites may be due to groundwater acidification by low-pH leachate from landfills [31]. Compared to the national technical regulation on groundwater quality, the pH in groundwater in the study areas was acceptable. In addition, the pH in groundwater in Ca Mau is also within the permissible level in drinking water prescribed by the Ministry of Health (2018) [32]. Former studies also measured pH values in groundwater. For example, pH in groundwater wells in the Ho Chi Minh City area was in the range of 3.4–7.4 [28], in the areas of Ba Ria – Vung Tau, it was 4.30–7.80 [19], and in the areas of Ha Nam Province, it was 6.19–7.33 [33]. A previous study also found that groundwater pH in the Mekong Delta of Vietnam was in the range of 6.54–7.76 [15]. Other studies from outside Vietnam found pH values in groundwater from 5.91 to 7.24 [3], between 7.03 and 8.50 [9], and in the range of 6.76–9.56 [34]. pH in groundwater may be acidic or alkaline, depending on the presence of chemical composition. The age of groundwater, mineralogy of aquifer materials, and geochemistry of groundwater systems have a strong influence on pH in groundwater [35].

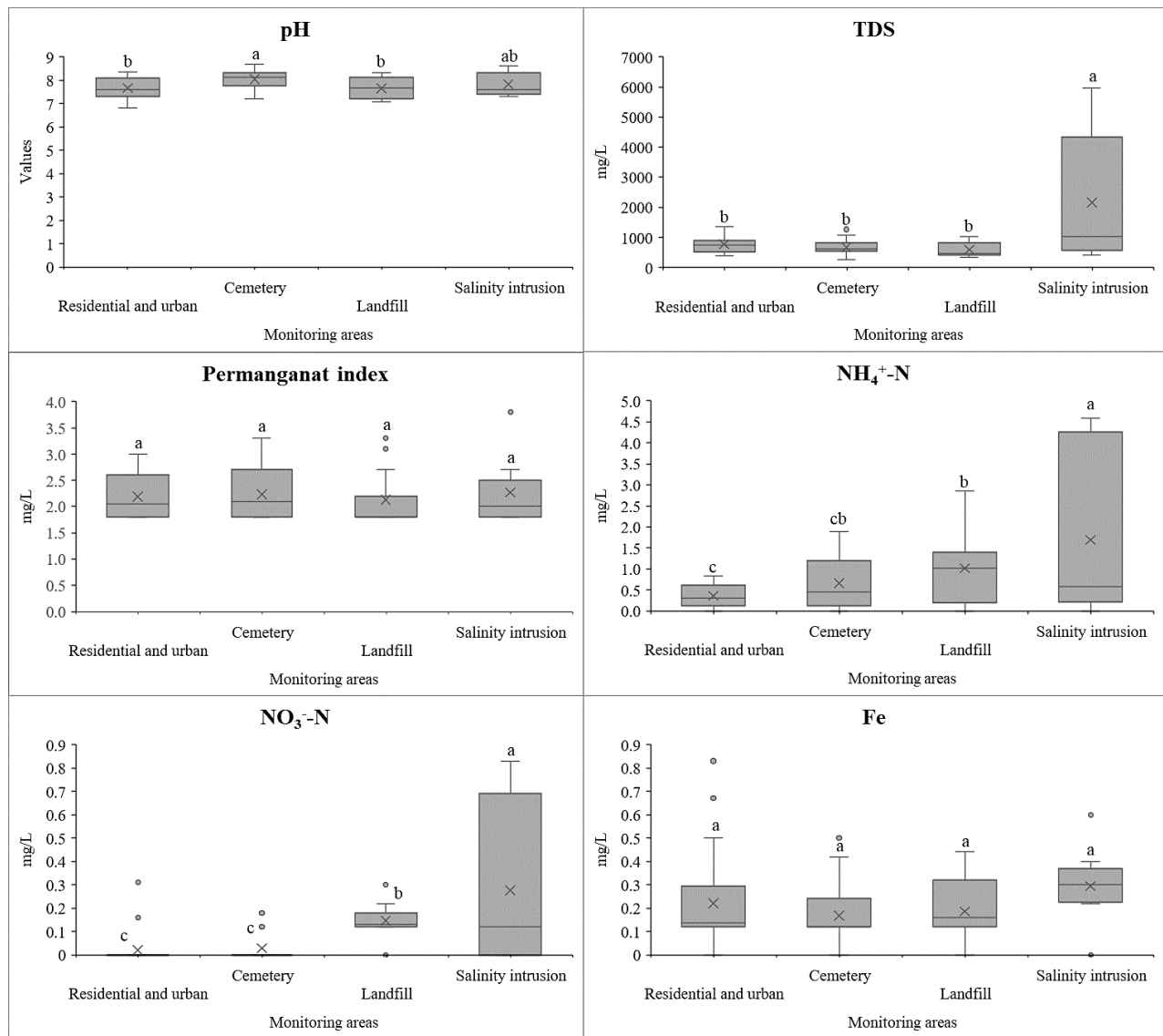


Figure 3. Spatial variations of groundwater parameters in the study areas

The total dissolved solids (TDS) concentration in groundwater in the study area was relatively high; there was a large variation between the sampling areas. The TDS concentration reached the minimum value of 588.07 ± 227.38 mg/L at the landfill area and reached the maximum value of 2153.11 ± 2113.31 mg/L in the area affected by saline intrusion (Figure 3). Statistical analysis results showed that TDS concentration in groundwater in areas affected by salinity intrusion was significantly different ($p < 0.05$) than that from the remaining areas (Figure 3). This result indicated that groundwater in certain areas of Ca Mau Province is influenced by salt concentration. A former study found that coastal aquifers could be influenced by seawater intrusion and the horizontal movement of saline water [36]. A former study found that groundwater in the Mekong Delta had TDS values of 544–4194 mg/L [15]. In coastal areas, TDS in groundwater was found at 281–8055 mg/L in Soc Trang province [18, 37] and 286–715 mg/L in Bac Lieu province [38]. In the Mekong Delta of Vietnam, high TDS could be associated with the impact of agrochemicals, wastewater leachate, and saline intrusion. Outside Vietnam, TDS in groundwater was measured at concentrations of 149.76 ± 132.66 – 202.33 ± 211.60 mg/L [3], 223 – 1372 mg/L [13]. As can be seen, TD varies spatially. TDS concentrations depend on groundwater aquifer characteristics, pollution sources, and saline water intrusion. TDS is used as a factor for the classification of groundwater into fresh hard water and medium salt hard water [39]. Compared with QCVN 09-MT:2015/BTNMT [27], TDS concentrations in groundwater in residential-urban areas, cemeteries, and landfilling sites were still within the allowable limits, while the TDS in the area affected by saline intrusion exceeded the allowable limit by 1.4 times.

Permanganate index (PI) is often used as an indicator to assess the pollution level of dissolved organic compounds in water. A high permanganate index indicates that the water has been contaminated with organic substances [40]. In this study, PI ranged from 2.13 ± 0.5 to 2.27 ± 0.65 mg/L, averaged at 2.2 ± 0.47 mg/L (Figure 3). The values of PI in groundwater in all sampling areas were not statistically significant ($p > 0.05$) (Figure 3). Compared with QCVN 09-MT:2015/BTBMT [27], PI in all groundwater samples was less than 4 mg/L, within the allowable limit. However, PI in

groundwater in the study area exceeded the limit value in the regulation of QCVN 01-1:2018/BYT (PI = 2 mg/L) [32]. This could mean that the groundwater in the study area is organically contaminated and unsuitable for drinking. The former study measured PI in groundwater, and it was found to be lower than that of the present study. Hung et al. (2018) [41] found PI of 0.17 ± 0.0058 – 2.63 ± 0.058 mg/L in groundwater in Trang Bang district, Tay Ninh province, while PI measured at 0.47 ± 0.15 – 0.63 ± 0.25 mg/L in groundwater in Pleiku city, Gia Lai province [42]. The variation of PI in groundwater could be attributed to the presence of microorganisms due to the occurrence of nutrients [43]. The death of microorganisms could consequently release organic matter, resulting in PI variation. In addition, dissolved organic matter from agricultural and landfill areas could also percolate into groundwater, resulting in high PI [44, 45].

Figure 3 shows that NH_4^+ -N concentrations in groundwater in the study areas in the range of 0.36 ± 0.26 to 1.69 ± 2.03 mg/L and averaged 0.76 ± 0.94 mg/L. The highest NH_4^+ -N concentrations in groundwater were found in areas influenced by saline intrusion, while the lowest were found in residential-urban areas. NH_4^+ -N concentrations in the areas of landfill and saline intrusion exceeded the limit of QCVN 09-MT:2015/BTNMT [27] by 1.01 and 1.69, respectively. Notably, the concentration of NH_4^+ -N in all monitored impact areas exceeded the allowable limit of QCVN 01-1:2018/BYT [32] by 1.2 to 5.6 times on the quality of clean water used for domestic purposes. Sources of NH_4^+ -N contaminating groundwater could be inappropriate discharges of waste and wastewater from domestic and industrial activities, landfill leachate, and the application of fertilizers in agriculture [15, 20, 23, 28, 37, 46]. NH_4^+ -N in groundwater was found up to 28.2 mg/L in Duy Tien district in Ha Nam province [33], at 16,086 mg/L at Xuan Mai town in Hanoi [47], and at 57.3 mg/L at Valley Kathmandu in Nepal [48]. Other studies found NH_4^+ -N concentrations in groundwater in the Mekong Delta, Vietnam, at 0.24–10.8 mg/L [18], 0.07–2.55 mg/L in An Giang groundwater [24], and 0–7 mg/L in Tra Vinh groundwater [23]. High concentrations of NH_4^+ -N in groundwater cause an unpleasant taste and odour, reduce the chlorination effect, and increase the likelihood of pathogen contamination during water distribution [7]. High levels of NH_4^+ -N in the human body could lead to blue baby syndrome, liver damage, and stomach cancer [46].

The concentrations of NO_3^- -N ranged from 0.02 ± 0.07 mg/L to 0.28 ± 0.35 mg/L, and the average value was 0.08 ± 0.16 mg/L (Figure 3). The highest concentration of NO_3^- -N was found in groundwater samples influenced by saline intrusion. Meanwhile, the lowest concentration of NO_3^- -N was found in the saline intrusion areas. NO_3^- -N was also found in groundwater in the Vietnamese Mekong Delta in several former studies. The mean in NO_3^- -N in the provinces of An Giang, Dong Thap, and Kien Giang were 0–1.32 mg/L, 0.73–2.23 mg/L, and 0–0.60 mg/L, respectively [15], in groundwater in Soc Trang province was 0.1–0.260 mg/L. This study found that NO_3^- -N concentrations in all sampling wells are within the limits of QCVN 09-MT:2015/BTNMT (15 mg/L) [27] and QCVN 01-1:2018/BYT (2 mg/L) [32]. Sources of NO_3^- -N variation in groundwater may be from nitrogen fertilizer application, livestock waste, landfill leachate, and industrial waste [20, 23, 49]. The nitrate concentration in groundwater found in this study was lower than in other studies. However, some other studies have found that nitrate is very high in groundwater. NO_3^- -N concentrations were found at 1.94 to 5.89 mg/L in the northeast part of Chengdu Plain in the Sichuan Basin [20] and at 0.12–11.51 mg/L in Uva province, Sri Lanka [30]. Groundwater with a high concentration of nitrate could result in health issues such as gastric cancer, birth malformation, hypertension, and methemoglobinemia [23, 50].

Iron is often dissolved in groundwater, causing the water to have scale, color, and an unpleasant taste [51]. In the Ca Mau peninsula, the Fe concentration in groundwater was very low, ranging from 0.17 ± 0.13 mg/L to 0.29 ± 0.16 mg/L, with an average of 0.2 ± 0.17 mg/L. The statistical analysis showed that the Fe concentration at four different impact areas was not statistically significant ($p > 0.05$) (Figure 3). The former study reported that Fe in groundwater in some provinces in the Mekong Delta, Vietnam, was 0.02 ± 0.02 to 3.38 ± 1.09 mg/L [15]. Groundwater in Soc Trang province had a significant concentration of Fe (0.04–19.8 mg/L, averaged at 2.17 mg/L) [37]. Other studies also found high Fe concentrations in groundwater [28, 33, 51]. The Fe concentration in groundwater in the former study was higher than that in the current study. The source of Fe formation in groundwater is mainly natural, such as the weathering of iron-rich minerals (hematite, goethite, magnetite, and siderite) [52]. However, the hydroxylation of iron ions occurs under anaerobic conditions, leading to iron formation in water [53]. Fe concentrations in groundwater in the study area were still within the allowable limit of QCVN 09-MT:2015/BTNMT [27]. However, Fe at the saline intrusion areas was exceeding the limit of QCVN 01-1:2018/BYT (0.3 mg/L) [32]. Fe at high concentrations (> 0.3 mg/L) causes human health risks such as hemochromatosis, leading to organ damage, cirrhosis, hepatocellular carcinoma, and hemosiderosis [53].

3.2. Potential Sources of Groundwater Quality Change

Principal component analysis showed that two main sources have an influence on groundwater in the study area (Figure 4 and Table 4). In this study, the retained PCs to explain the groundwater quality change had Eigenvalues greater than 1 [14, 53]. Two PCs were formed in residential-urban areas, cemeteries, landfills, and areas affected by the saline intrusion, explaining 79.6%, 85.2%, 89.2%, and 100% of the total variance, respectively. According to Elemile et al. (2021) [3], a total variance of PCs greater than 70% is acceptable. At the same time, the study examined the relevance of PCA through the Kaiser-Meyer-Olkin index (KMO) and Bartlett test. The significant KMO value means that the factor analysis is appropriate and the Bartlett test is statistically significant ($p < 0.05$); the observed variables are

correlated with each other in the population. Analysis results at each impact area, including residential-urban areas (KMO = 0.633; $p = 0.01$), cemetery (KMO = 0.5; $p = 0.00$), landfills (KMO = 0.544; $p = 0.00$), and areas affected by saline intrusion (KMO = 0.5; $p = 0.00$), indicated that all the values of KMO were equal to or greater than 0.5 and the p -value was less than 0.05. So, the results of the PCA analysis were suitable.

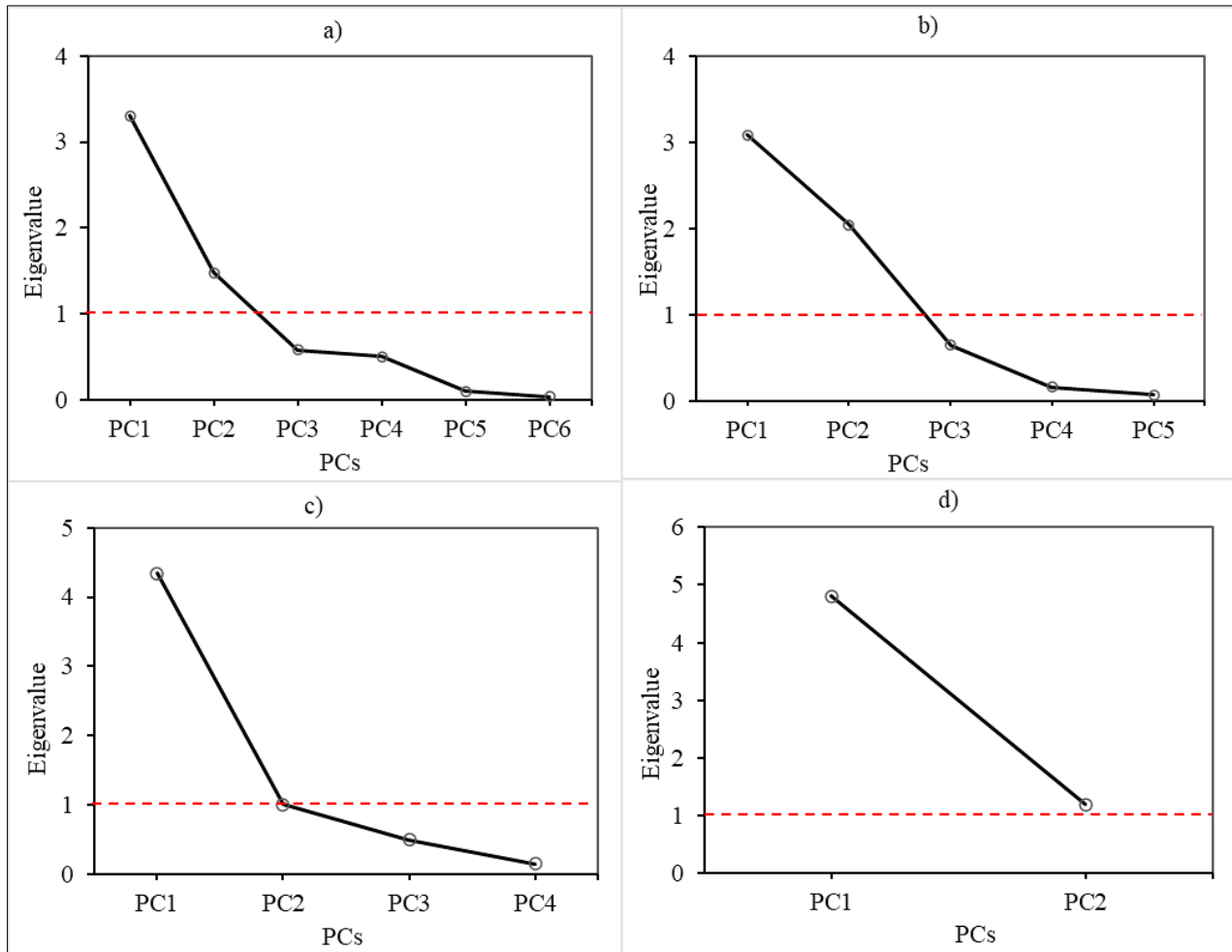


Figure 4. Scree plots for the principal component analysis

Table 4. Key variables influencing groundwater quality in the study area

Parameter	Residential and urban		Cemetery		Landfill		Salinity intrusion	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
pH	-0.396	-0.203	0.515	-0.243	-0.410	0.149	0.261	-0.753
TDS	0.433	-0.417	0.436	0.387	-0.452	0.160	-0.433	-0.286
PI	0.450	0.222	0.420	0.343	-0.451	-0.079	-0.415	-0.381
NH ₄ ⁺ -N	0.501	0.080	-0.453	0.180	-0.410	-0.479	-0.452	-0.116
NO ₃ ⁻ -N	0.332	-0.638	0.110	0.657	-0.446	-0.215	-0.454	-0.077
Fe	0.303	0.567	-0.389	0.458	0.238	-0.819	-0.402	0.431
Eigenvalues	3.30	1.48	3.08	2.04	4.34	1.01	4.81	1.19
% Variation	55.00	24.60	51.30	34.00	72.40	16.90	80.20	19.80
Cum. % Variation	55.00	79.60	51.30	85.20	72.40	89.20	80.20	100

In the residential-urban area, the first principal component (PC1) is the most crucial component, explaining 55% of the total variance of six groundwater quality variables, with moderate loading values to NH₄⁺-N (0.501) and weak to pH (-0.396), TDS (0.433), PI (0.450), NO₃⁻-N (0.332), and Fe (0.303). The possible source of pollution can be domestic wastewater since it contains high concentrations of TDS, C, N, and P [54, 55]. Iron oxides in the soil layer can be leached and reduced by organic matter under anaerobic conditions, leading to the formation of Fe in groundwater [28]. Therefore, PC1 could be from internal and external causes of groundwater pollution. The second component (PC2), which

explained 24.60% of the total variance of the groundwater quality dataset, had a mean loading factor of NO_3^- -N (-0.638) and Fe (0.567). The concentration of Fe in groundwater in urban residential areas was relatively low, possibly due to natural causes such as the weathering of iron-rich minerals in rocks [52]. Similarly, the concentration of NO_3^- -N was only recorded to be very low at GW3 and GW8, possibly because nitrogen metabolism occurred in suitable environmental conditions, which converted NH_4^+ -N into NO_3^- -N.

In the cemetery area, PC1 formed a moderate correlation to pH (0.515), weak to TDS (0.436), PI (0.420), NH_4^+ -N (-0.453), and Fe (-0.389). PC1 explained more than 51% of the total variance of the groundwater quality parameters. Pollutants generated from old cemeteries could contaminate the soil and seep into groundwater [56]. PC2 explained 34% of the total variance and was positively related to NO_3^- -N (0.657). Nitrogen, especially in the form of nitrate, is one of the main pollutants from decomposing corpses and can have a negative impact on the environment [57]. Nitrogen is one of the main components of protein in the human body, so nitrogen can enter groundwater through leachate generated after human body decomposition [58]. In addition, the groundwater affected by the cemetery area also has high pH and TDS values [58]. At the same time, PC2 also explained that it had a weak correlation with TDS (0.387), permanganate index (0.343), and Fe (0.458). This result showed that natural sources also contributed to the TDS and Fe concentrations.

At the landfill site, the first PC was correlated with most groundwater quality parameters, explaining more than 72% of the total variance. PC1 formed a weak correlation with pH (-0.410), TDS (-0.452), permanganate index (-0.451), NH_4^+ -N (-0.410), and NO_3^- -N (-0.446). While the second PC explained almost 17% of the total variance, it was mainly strongly correlated with Fe (-0.819). The source of groundwater pollution in this area may come from leachate, the decomposition of organic matter in waste streams. Open-air, unsorted, and uncoated landfills could lead to leachate seeping directly into the soil and entering groundwater vertically. Leachate from landfills represents a serious threat to groundwater quality as it contains a wide range of contaminants. Typically, very high and fluctuating concentrations of BOD, COD, NH_4^+ -N, Fe^{2+} , and TDS were in the range of 10,000–25,000 mg/L, 15,000–40,000 mg/L, 1500–4250 mg/L, 500–1500 mg/L, and 10,000–25,000 mg/L, respectively [59]. In this study, the concentration of NH_4^+ -N in groundwater in the area affected by the landfill exceeded the allowable limit of QCVN 09-MT:2015/BTNMT. The status of leachate contaminating groundwater has been reported in several areas [59–61]. In addition, unclassified waste burying could contribute to Fe accumulation in the soil and negatively affect groundwater quality in the study area.

In the area affected by saline intrusion, PC1 was the most important component, explaining more than 80% of the total variance of the groundwater quality parameters. PC1 formed correlations with most groundwater variables, such as TDS (-0.433), permanganate index (-0.415), NH_4^+ -N (0.452), NO_3^- -N (0.454), and Fe (-0.402), at weak levels. The high TDS concentration in groundwater samples in coastal areas is mainly derived from intrusive seawater [36]. TDS pollution can be caused by domestic and industrial wastewater, sewage pipe leaks, and the dissolution of mineral-bearing rocks. High concentrations of TDS and exceeding the allowable limit of QCVN 09-MT:2015/BTNMT were recorded in this area. In addition, this area had the highest concentrations of NH_4^+ -N, NO_3^- -N, permanganate, and Fe. Sources of pollution could come from domestic and industrial wastewater. Meanwhile, PC2 strongly correlated with the pH parameter (-0.753), explaining about 20% of the total variance. The pH value was greater than 7 in most of the groundwater monitoring stations, which was caused by saline intrusion in the coastal area, which increases strong basic salts and weak acids in aquifers.

PCA results indicated that two main sources are causing groundwater variation in the residential-urban area: the cemetery area, the landfilling area, and the saline intrusion area. All the observed groundwater parameters (pH, TDS, permanganate index, NH_4^+ -N, NO_3^- -N, and Fe) play key roles in representing groundwater quality in the study area and thus should be monitored. Potential polluting sources of groundwater in the study areas could be domestic and industrial wastewater discharge, leachate from cemeteries and landfills, the nature of groundwater aquifers, and seawater intrusion.

3.3. Classification of Groundwater Quality in the Study Area

In the study, the groundwater quality index (GWQI) was calculated from six variables (pH, TDS, permanganate index, NH_4^+ -N, NO_3^- -N, and Fe) to provide information regarding the overall quality of the groundwater (Figure 5). Groundwater quality in the study area was divided into four categories: (1) excellent, (2) good, (3) poor, and (4) very poor. In which, groundwater samples with excellent and good water quality accounted for the majority, with GWQI index values ranging from 31–40 and 50–86, respectively. There were a total of 21 groundwater samples with excellent water quality (accounting for 44% of the total) and good water quality (accounting for 40% of the total), including 8 groundwater samples (GW1-GW8) in residential-urban areas, 7 groundwater samples (GW9, GW10, GW11, GW13, GW15, GW16, and GW17) in the cemetery area, 4 samples of groundwater (GW18-GW22) at the landfill site, and 2 samples of groundwater (GW23 and GW24) in the affected area. At these locations, most of the groundwater parameters reached the allowable limit of QCVN 09-MT:2015/BTNMT [27]. Groundwater quality at these locations can be used for drinking purposes, but it must be treated accordingly. For poor water quality, there were three locations (accounting for 12% of the total), including GW12, GW14 in the cemetery area, and GW21 in the landfill area. These three locations had NH_4^+ -N concentrations that exceeded the limit of QCVN 09-MT:2015/BTNMT by 1.3–2.3 times. The groundwater quality at the location GW24 (in the saltwater intrusion area) was very poor and not recommended for drinking purposes.

TDS and $\text{NH}_4^+\text{-N}$ exceeded the limits of QCVN 09-MT:2015/BTNMT by 3.3 times and 4.4 times, respectively. The causes of groundwater pollution at the GW24 site may be due to seawater intrusion and improper wastewater and waste management. Compared with other studies, the overall groundwater quality in Ca Mau was better than that in Ha Nam province (GWQI 67–369) [33], but it was worse than the groundwater quality in Ba Ria – Vung Tau [19] and the groundwater quality in Dong Thap, An Giang, Hau Giang, and Kien Giang [15]. The difference in results of GWQI in various areas in the current and former studies could be from the input data. More groundwater quality parameters should be added to the calculation of the GWQI in the future at the study areas for groundwater quality evaluation.

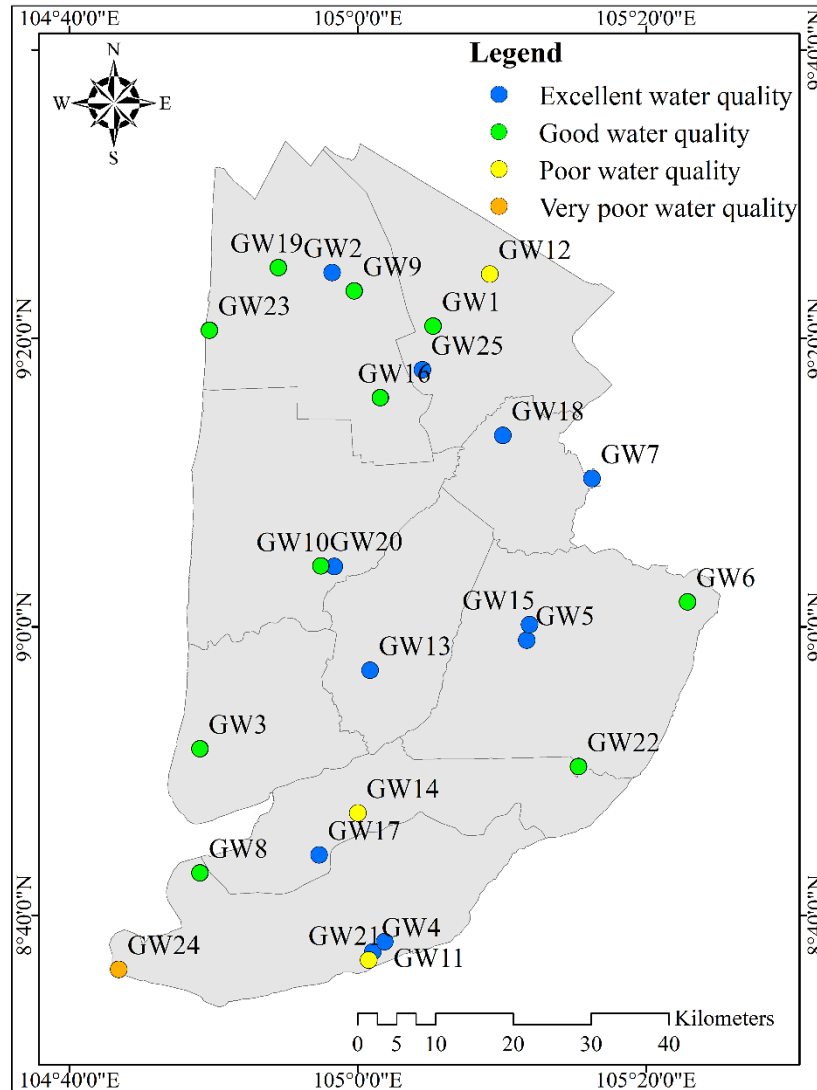


Figure 5. Map of groundwater quality classification

Four groups of groundwater quality were formed as the result of cluster analysis (Figure 6). Group I represented groundwater with the worst water quality, including site GW24 (4% of the total). This result is similar to the GWQI index result; this is a location with "very bad" water quality with TDS and $\text{NH}_4^+\text{-N}$ concentrations exceeding the permissible limit of QCVN 09-MT:2015/BTNMT 3.3 times and 4.4 times, respectively. Group II represented groundwater of medium quality, including site GW12 (4% of the total). Group II groundwater quality had a high ammonium concentration (1.6 times higher than the limit of QCVN 09-MT:2015/BTNMT). Group III gathered several locations with the most similar groundwater characteristics, with 14 sites (56% of the total) in residential areas, urban areas, cemeteries, and areas affected by saline intrusion (GW1, GW2, GW3, GW4, GW5, GW6, GW7, GW8, GW10, GW11, GW13, GW15, GW17, and GW25). Group III was the group with the lowest concentration of groundwater pollutants and was within the allowable limits of QCVN 09-MT:2015/BTNMT. Similarly, the groundwater quality of Group IV was still unpolluted, and the concentrations of groundwater pollutants were still within the allowable limits of QCVN 09-MT:2015/BTNMT. However, the concentration of $\text{NH}_4^+\text{-N}$ in groundwater was at an alarming level, close to 1 mg/L. Group IV gathered 9 locations, including GW9, GW14, GW16, GW18, GW19, GW20, GW21, GW22, and GW23, belonging to cemeteries, landfills, and areas affected by saline intrusion. CA results revealed that there is possible to reduce sampling sites in residential-urban areas, cemetery areas, and landfill areas. Cluster III comprised eight sites in residential-urban areas, which could mean that the groundwater quality in this area is relatively uniform. The study

result suggests reducing 4 out of 8 sites from residential-urban areas but still remaining representative of groundwater quality monitoring. In addition, there were four sites (GW10, GW11, GW13, and GW17) in the cemetery grouped in the same Cluster III, and two of these four sites could be considered to be removed from the current monitoring program. For the landfill area, the five sites of GW18, GW19, GW20, GW21, and GW22 were clustered in Group IV, and these sites could be reduced by three sites (GW20, GW21, and GW22). CA recommends reducing 9 out of 25 sites from the current monitoring program.

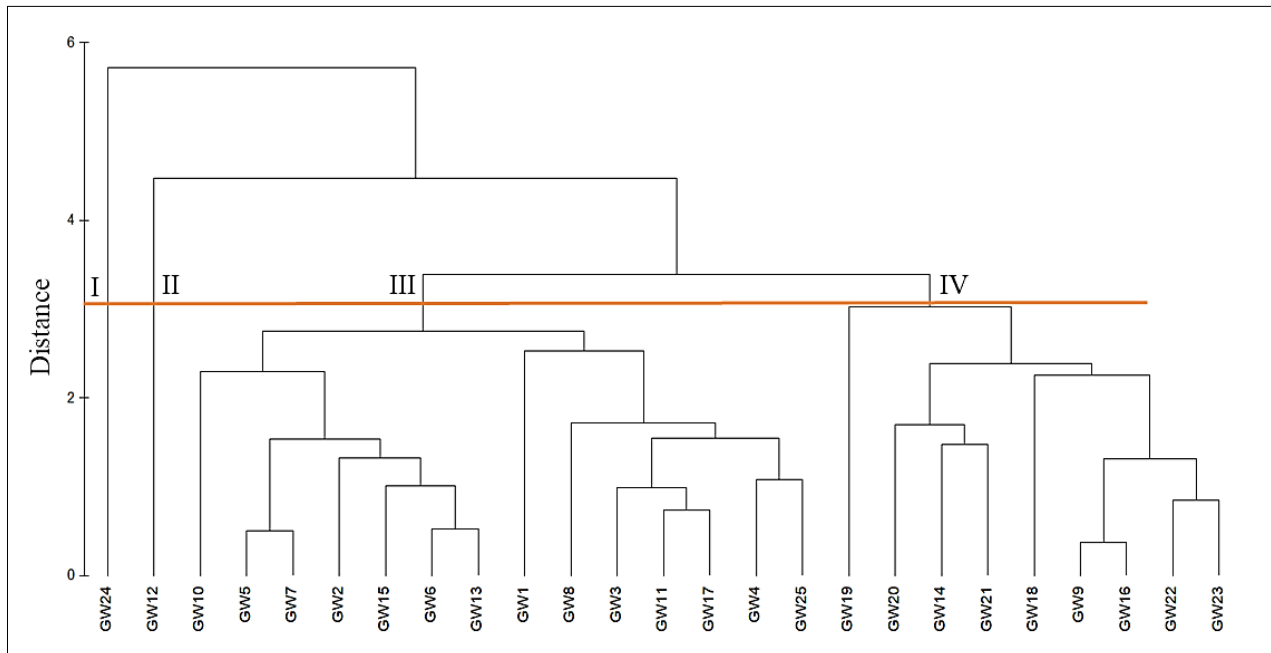


Figure 6. Clustering groundwater quality in the study area

4. Conclusion

The present study examined groundwater quality in residential-urban areas, cemetery areas, landfilling areas, and saline intrusion areas in Ca Mau Province, Vietnam. The results revealed that groundwater in the landfilling area was contaminated by $\text{NH}_4^+\text{-N}$, and the groundwater quality in the saline intrusion area was polluted by TDS and $\text{NH}_4^+\text{-N}$. The groundwater quality index classified groundwater into four categories (i.e., excellent, good, poor, and very poor water quality), accounting for 44%, 40%, 12%, and 4% of the total samples, respectively. $\text{NH}_4^+\text{-N}$ and TDS represented groundwater parameters that contribute to poor and very poor quality. Cluster analysis divided groundwater quality into four groups, of which Group I had the lowest quality. PCA results indicated two main sources causing groundwater variation in each residential-urban area: the cemetery, landfilling, and saline intrusion areas. All the observed groundwater parameters (pH, TDS, permanganate index, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Fe) play key roles in representing groundwater quality in the study area and, thus, should be monitored in the future. However, more groundwater quality parameters (for examples, chloride, arsenic, hardness, bicarbonate, etc.) should be added to the monitoring program. Potential polluting sources of groundwater in the study areas could be domestic and industrial wastewater discharge, leachate from cemeteries and landfills, the nature of groundwater aquifers, and seawater intrusion. The current study's results suggest reducing 9 groundwater sampling locations while still ensuring groundwater quality monitoring representative. The current findings provide scientific information for local environmental authorities to manage and monitor groundwater quality in the study area.

5. Declarations

5.1. Author Contributions

Conceptualization, N.T.G. and P.Q.N.; methodology, N.T.G. and P.Q.N.; software, N.T.G.; validation, P.Q.N.; formal analysis, N.T.G. and P.Q.N.; investigation, N.T.G.; resources, N.T.G. and P.Q.N.; data curation, N.T.G. and P.Q.N.; writing—original draft preparation, N.T.G. and P.Q.N.; writing—review and editing, N.T.G. and P.Q.N.; visualization, N.T.G. and P.Q.N.; supervision, N.T.G. and P.Q.N.; project administration, N.T.G. and P.Q.N.; funding acquisition, N.T.G. and P.Q.N. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available in the article.

5.3. Funding

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5.5. Conflicts of Interest

The authors declare no conflict of interest.

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