



KEY FACTORS DOMINATING THE GROUNDWATER CHEMICAL COMPOSITION IN BA RIA - VUNG TAU PROVINCE

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Abstract

In Ba Ria - Vung Tau province, this study has determined that the dominant factors influencing the hydro-chemical composition of fractured aquifers are the replenishment of meteoric water, coupled with the processes of dissolution and leaching of Ca^{2+} and Mg^{2+} from weathered basaltic rocks (olivine and plagioclase minerals). Additionally, the exchange process contributes to the enrichment of Na^+ by replacing Ca^{2+} and Mg^{2+} . In porous aquifers, the central-to-sea cross-section highlights meteoric water dominance from rain and surface sources. Groundwater undergoes exchange-absorption with silicate minerals, enriching Ca^{2+} and Mg^{2+} (reducing Na^+). Seaward, dissolution and leaching of salts in marine-origin sediments (mQ_2 , mQ_1^3 , mQ_1^{2-3} , and mN_2) prevail. The results of this paper provide necessary information for the effective management of groundwater quality.

Keywords: Chemical composition of groundwater; Leaching-dissolution process; Exchange-absorption process; Saltwater intrusion process.

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1. Introduction

Groundwater plays an essential role in all human development activities, particularly in coastal areas where good-quality water is scarce. Therefore, the chemical composition of groundwater is a top priority. Based on the limited concentrations of chemical parameters that can cause harm to human health when groundwater is directly used for various purposes, the Ministry of Natural Resources and Environment (MONRE) has recently issued the National Technical Regulation on Groundwater Quality (QCVN 09:2023/BTNMT). This

standard is applied to assess and monitor groundwater quality, providing a basis for guiding various water use purposes.

In Vietnam, the chemical composition of groundwater has been studied as part of hydrogeological mapping carried out in various regions across the country. Specifically, in the vicinity of the Ba Ria - Vung Tau province, the Department of Geology and Minerals of Vietnam (DGMV) has conducted groundwater studies at a scale of 1:50,000 in locations such as Ho Chi Minh city, Bien Hoa - Long Thanh, Long Thanh - Vung Tau, and others. The results

include the creation of hydrogeochemical maps accompanied by cross-sections that focus on overall mineralization and the distribution characteristics of six major ions. Preliminary assessments have also been conducted regarding the potential sources of these main ions and saltwater intrusion. In-depth research on the origin and formation of the chemical components of groundwater in Neogene and Quaternary deposits has been carried out in various locations, including the coastal areas of the North and North Central regions [5], the Mekong delta [4], etc. The main content of these studies comprises integrated results of various processes that have occurred during the existence and movement process in porous media of soils and rocks. However, due to the wide scope of implementation and a limited number of samples, the detailed interactions between water and rock or soil have not been fully represented. The formulation of the chemical composition of groundwater has been studied by scientists worldwide [6, 7, 8, 9, 10] Saltwater intrusion is also a contributing

factor to the formation of key chemical components. In Ba Ria -Vung Tau province, studies have been conducted in the exploration and exploitation activities, such as in Ba Ria with a capacity of 13,000 m³/day and My Xuan with 15,000 m³/day. In fact, in exploiting the aquifer n₂² for nearly 20 years, the saltwater intrusion process has not occurred significantly even though the well site is not far from the saline boundary.

Based on research on the structural characteristics of the groundwater system and the current water quality data available in the database of the Ba Ria - Vung Tau province (under DONRE), this paper conducts synthesis, processing, analysis, and evaluation to determine the processes of formation of key elements Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, Cl⁻, and SO₄²⁻ under natural conditions for each aquifer.

The content presented in this paper is not only about scientific research but also provides important information that contributes to the sustainable management of groundwater quality.

2. Study area

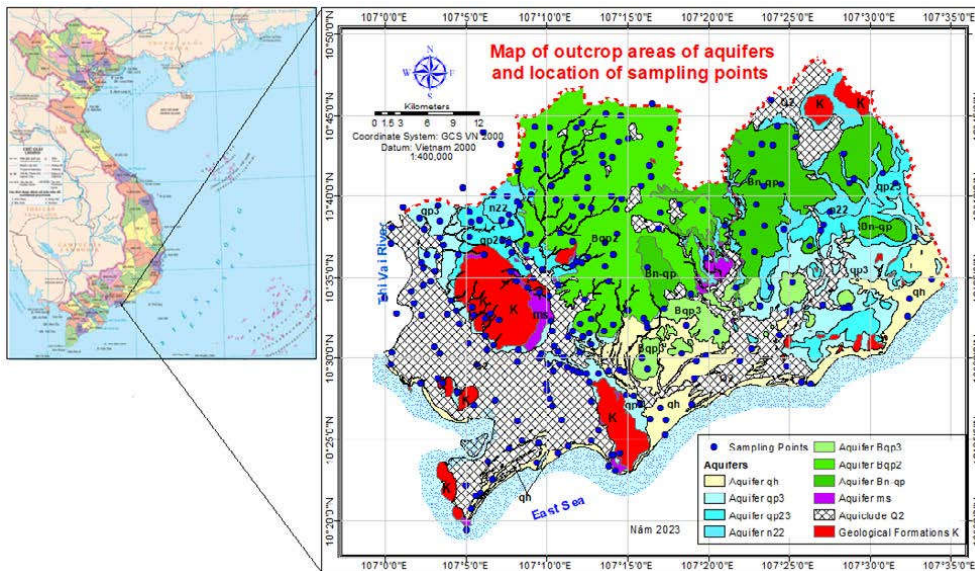


Figure 1: Study area location and Outcrop areas of aquifer locations

Ba Ria - Vung Tau is a small coastal province with an area of about 2,000 km², but it has a rather specific hydrogeological structure, typical of many areas in Southern Vietnam (Fig.1). There are basaltic blocks intercalated with (N-Q) sediments, overlying terrigenous sediment beds (Eastern Nambo Plain); an accumulative plain of Quaternary sediments (coastal area of South Trung Bo) and an accumulative plain of Neogene-Quaternary sediments (Mekong plain). Accompanying this structure, extrusive activities of magmatic blocks have formed mountains and economically valuable mines of thermal and mineral water (Binh Chau, Suoi Nghe). As a result, aquifers have been formulated containing water of various chemical compositions, creating a complicated hydrochemical picture within a small area (Fig.1).

2.1. Fractured aquifers

In the study area, there are four fractured aquifers, including the upper Pleistocene basalt aquifer (β_{qp3}), the Pliocene-Pleistocene basalt aquifer (β_{n-qp}), the middle Pleistocene basalt aquifer (β_{qp2}), and the Mesozoic aquifers in terrigenous sedimentary rocks (ms). The ms aquifer is present throughout the region with a very high thickness, unlike the others. The remaining three aquifers are exclusively found in the central part of the region, covering Chau Duc, Northern Xuyen Moc, Dat Do, and Long Dien. The thickness of these aquifers decreases towards the distribution boundaries and progressively increases towards the center of the basalt blocks, ranging from a few dozen to over 100 m. The spatial and depth distribution characteristics of these aquifers are illustrated in Fig. 1 and Fig. 2.

2.2. Porous aquifers

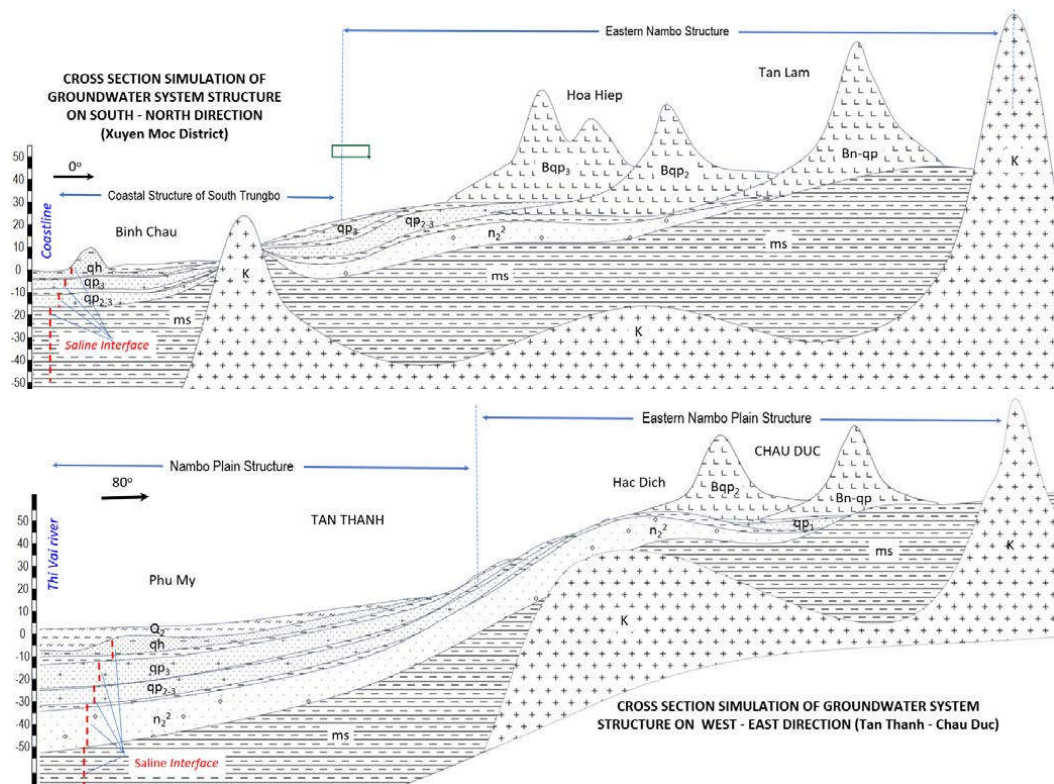


Figure 2: Unavailable illustration of scale cross-section for the regional hydro-geological structure [2]

In the research area, there are four primary porous aquifers. In order from top to bottom, the aquifer in Holocene deposits (qh), the aquifer in upper Pleistocene deposits (qp₃), the aquifer in middle-upper Pleistocene deposits (qp₂₋₃), and the aquifer in middle Pliocene deposits (n₂²). The thickness of them generally increases from the central towards the sea, with the greatest thickness found in Vung Tau city. The qh and qp₃ have a maximum thickness of about 10 - 15 m, while the qp₂₋₃ and n₂² reach 25 - 40 m. The lithology of these aquifers is quite similar, mainly composed of fine to medium sand, occasionally coarse sand, and interbedded with gravel. Intermittently, there are layers of fine silt, sandy clay, or clayey silt with a relatively small thickness, creating discontinuous geological windows. The distribution characteristics on the surface and in cross-sections are illustrated in Fig.1 and Fig.2.

3. Study method and approach

3.1. Applied data

The article utilizes a dataset of groundwater chemical composition from previous projects conducted by DGMV. This data is stored in the groundwater database at DONRE of Ba Ria - Vung Tau province [2] and additional data from recent projects [1, 2, 3]. Samples were collected from research boreholes, monitoring boreholes, exploitation boreholes, or dug wells during the dry season each year, following current technical regulations. The sampling locations are illustrated in Fig. 1, and the statistical sample quantities are presented in Table 1.

The analysis method follows the procedures specified by the DGMV and is implemented by the affiliated associations. The main analysis parameters are pH, SiO₂, CO₂, water hardness, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, NO₂⁻, CO₃⁻ and dried residue (105 °C).

Table 1. Statistical samples by aquifers

TDS value (mg/l)	Number of samples aquifers							
	βn-qp	βqp ₂	βqp ₃	ms	n ₂ ²	qp ₂₋₃	qp ₃	qh
< 100	10	39	1	2	25	33	23	19
100 - 1,000	24	68	4	9	55	26	23	65
> 1,000	0	0	0	1	12	8	8	17
Total	34	107	5	12	92	67	54	101

3.2. Synthesis and evaluation methods

Step 1. Data adjustment: Data is exported from the database in the form of Excel tables. Check for analysis errors and eliminate samples with unreliable data.

Step 2. Check the information on aquifers and create tables of statistical samples.

Step 3. Calculate the values and chemical ratios then statistics into groups:

Group 1: rCa²⁺, rMg²⁺, rCl⁻ and SO₄²⁻;

Group 2: TDS, Cl⁻/(Cl⁻+HCO₃⁻) and Na⁺/(Na⁺+Ca²⁺);

Group 3: Cl⁻ and rNa⁺+rCl⁻.

Then, create diagrams: Piper, Gibbs, and Mercado. Moreover, to supply more needed information, this paper also creates some other diagrams such as rCa²⁺/rNa⁺ with rHCO₃⁻/rNa⁺; rCa²⁺/rNa⁺ with rMg²⁺/rNa⁺; rCl⁻ and rNa⁺; rCa²⁺ and rMg²⁺; rNa⁺/Cl⁻ and rCa²⁺/(HCO₃⁻+SO₄²⁻).

Step 4. Analysis and evaluation of results: Based on the distribution

characteristics and the lithological components of the water-bearing rock or soil, the study predicts the interaction processes between water and rocks or soils from the recharge zone, through the flow zone, to the discharge zone. The results are compared on the charts established in Step 3 to identify the predominant interaction processes

3. Results and discussion

3.1. Formulation origin of ions in fractured aquifers

Table 2 shows a statistical summary of the hydrogeochemical characteristics of each fractured aquifer. This sample set will be used for the presentation in the content below.

As seen in Fig. 3, aquifers ms, β n-qp, and β qp₃ show concentrated anions in zone

E, displaying a mixing process of fresh water and a predominant ion exchange role with an insignificant increase in Cl⁻ content. Meanwhile, anions are concentrated in zones B and D, showing a mixing process towards desalinization and ion exchange: Adsorption of Na⁺ from water and release of Ca²⁺ and Mg²⁺ from minerals constituting basaltic rocks (plagioclase, olivine, etc.). As a result, contents of Ca²⁺ and Mg²⁺ increased, and Na⁺ decreased in these aquifers. In the upper diamond, samples are concentrated mainly in zone I, characterized by a water type bicarbonate-calcium (or magnesium). Some samples fell to zone III, characterized by a water type bicarbonate sodium (with increased contents of HCO₃⁻ and Na⁺), due to mixing with meteoric and surface water towards desalinization.

Table 2. Statistical summaries of hydrogeochemical properties of fractured aquifers

Property	Value	TDS	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	Fe ²⁺	Fe ³⁺	NO ₃ ⁻
Aquifer β n-qp	Min	40.0	1.0	1.0	0.0	0.9	7.6	-	-	-	-
	Max	335.0	57.1	46.5	46.3	50.5	366.1	16.5	3.0	1.0	30.0
	Average	146.9	15.9	12.7	6.8	14.8	90.9	1.0	0.1	0.1	4.2
	St deviation	84.2	14.4	10.3	8.7	8.4	89.7	3.0	0.5	0.2	7.9
Aquifer β qp2	Min	25.0	0.4	1.2	-	5.3	6.1	-	-	-	-
	Max	427.0	100.6	42.1	60.4	156.6	366.1	38.0	0.4	1.4	62.1
	Average	161.6	16.7	13.4	10.3	18.5	100.8	4.3	0.0	0.0	4.6
	St deviation	114.1	22.3	11.0	12.7	31.7	104.3	5.7	0.1	0.2	9.6
Aquifer β qp3	Min	52.0	2.2	3.0	4.0	8.9	20.5	-	-	-	-
	Max	255.0	20.7	33.3	26.1	58.6	158.7	-	0.1	0.2	31.3
	Ave	169.8	11.2	18.4	9.9	22.8	82.2	2.2	0.0	0.0	10.4
	SD	75.6	7.1	13.9	9.3	20.4	61.0	3.5	0.0	0.1	13.4
Aquifer ms	Min	64.1	1.8	3.0	2.4	8.9	36.6	-	-	-	0.1
	Max	1,657.0	456.6	39.1	47.2	933.3	1,226.5	160.0	0.2	0.5	5.2
	Average	440.6	95.4	21.5	16.5	85.6	278.3	14.6	0.1	0.1	0.9
	St deviation	197.0	49.8	7.0	7.1	46.7	100.7	8.7	0.0	0.0	1.4

Aquifer β qp₂ also has a formulation source of ions due to a similar process. However, because of its wide distribution, there have been some particular changes. There are two main trends of change:

- Increase of SO₄²⁺ content in zone E and movement of many samples to zone F. Possibly, this is the place where the oxidation-redox process of sulfur minerals in basaltic rocks occurred (pyrite mineral (FeS₂) adding SO₄²⁺ and HCO₃⁻ constituents to water).

- Increase of Cl^- content: Occurs in the southern coastal area (Dat Do, Long Dien districts and South of Xuyen Moc district) due to an increase of Cl^- content in atmospheric and surface water. Aquifer Bqp₂ has a large distribution area and favorable conditions to receive recharge sources from meteoric and surface water, inducing an enriching process of Cl^- and HCO_3^- . On the Mercado diagram (Fig. 4) there are samples below the seawater line $r\text{Na}^+/\text{rCl}^- = 0.85$ (zone of saline intrusion), but chloride content $\text{Cl}^- < 200 \text{ mg/l}$, so it can not be considered as a saltwater intrusion. This leads to the appearance of samples in zone II, characterized for water type chloride-sodium, and in zone III, characterized for water type bicarbonate-chloride-sodium. In short, the chemical composition of water in fractured aquifers primarily originates from atmospheric-continental or continental environments.

On the Gibbs diagram, the origin of cations predominantly arises from the interaction between soil rocks and water (Fig. 5). Specifically, this is ion exchange during the exchange-adsorption process (increase of Ca^{2+} and Mg^{2+} or Na^+ contents). The genesis of anions primarily stems from the supplementation originating from meteoric and surface water, characterized by an enrichment of chloride ions, as well as the oxidation-reduction processes of minerals containing sulfur, leading to the release of sulfate ions (SO_4^{2-}) into the aquatic environment. Salinity intrusion was indeed observed in certain samples collected from the aquifer close to the coastline. On the Mercado diagram, basaltic aquifers were not intruded by salinity, but there is a slight signal of salinity intrusion because of a slight increase of Cl^- content at some places (Fig. 4).

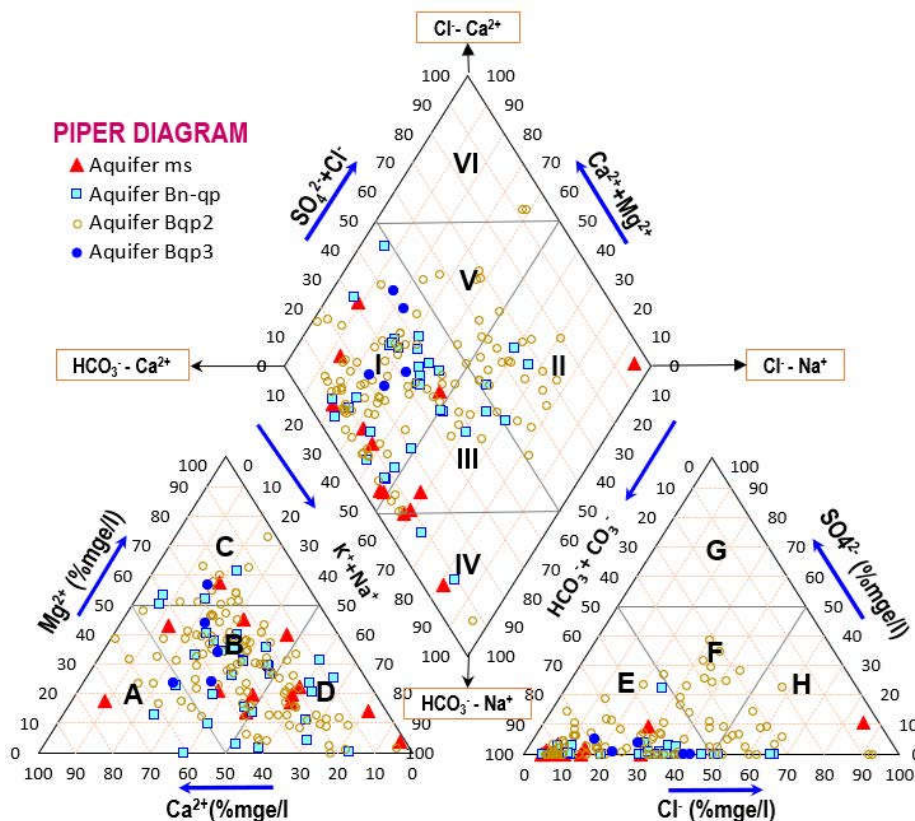


Figure 3: Piper diagram showing the chemical composition of fractured aquifers

In short, the chemical composition of water in fractured aquifers primarily originates from atmospheric-continental or continental environments. On the Gibbs diagram (Fig. 5), the origin of cations predominantly arises from the interaction between soil rocks and water. Specifically, this involves ion exchange during the exchange-adsorption process (increase of Ca^{2+} and Mg^{2+} or Na^+ contents). The genesis of anions primarily stems from the supplementation originating from meteoric and surface water, characterized

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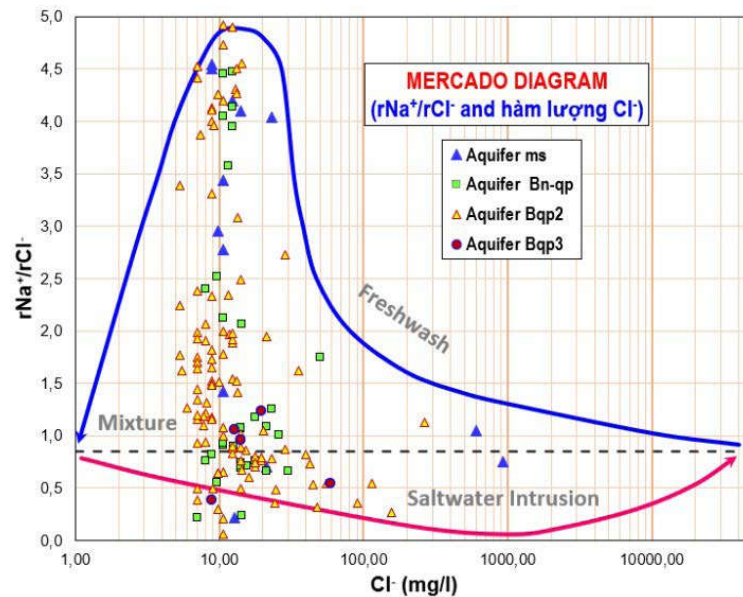


Figure 4: Mercado diagram showing chemical composition of fractured aquifers

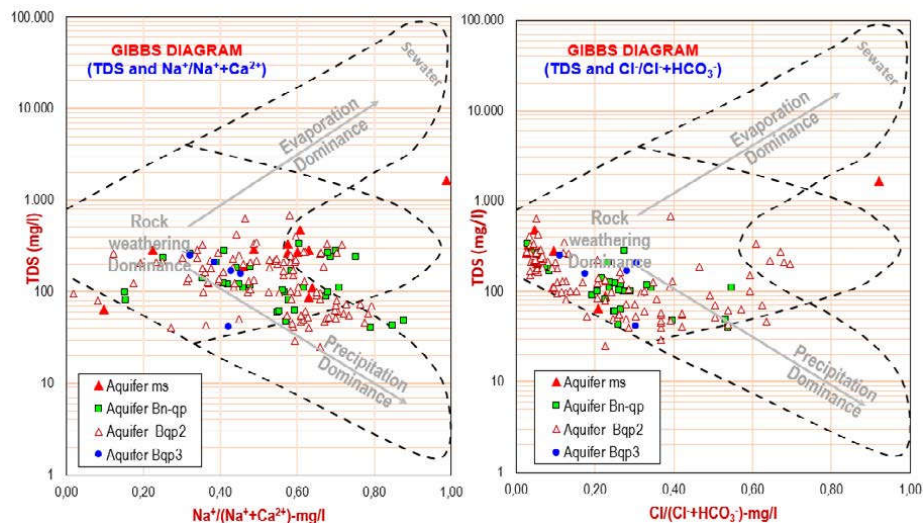


Figure 5: Gibbs diagram showing the chemical composition of fractured aquifers

3.2. Formulation origin of ions in porous aquifers

Table 3 shows a statistical summary of the hydrogeochemical characteristics of each fractured aquifer. This sample set will be used for the presentation of this content.

In Fig. 6, anions of aquifers qh are regularly distributed in zones E and F and concentrated in zone H. This shows the mixing process of fresh water, and the role of ion exchange is localized, while chloride content Cl^- changes rather complexly.

The cations of aquifer qh are concentrated in zone D, where the exchange process of Na^+ , Ca^{2+} and Mg^{2+} simultaneously occurs. In this circumstance, it is remarkable that many samples show the predominance of the exchange-enrichment process of Ca^{2+} and Mg^{2+} by their presence in zone B (some particular samples in zone A). This represents a mixing process towards enrichment of Na^+ from meteoric and surface water and ion exchange: Adsorption of Na^+ from water and release of Ca^{2+} and Mg^{2+} from clay minerals. As a result, the contents of Ca^{2+} and Mg^{2+} increased and the content of Na^+ decreased in the water of these aquifers. In the upper diamond, samples are concentrated mainly in zones I and II. These zones are characterized by water types bicarbonate-calcium (or magnesium) and bicarbonate chloride-sodium and chloride-sodium. Some samples fall in zone III, characterized for water type bicarbonate-sodium (with increased contents of HCO_3^- and Na^+) due to the mixing process with meteoric and surface water towards desalinization. Some other samples are concentrated in zone V, characterized for water type bicarbonate sulfate-sodium or chloride

sulfate-sodium. The swamp process in low, depressed areas was also involved.

Meanwhile, cations of aquifer qp₃ are concentrated in zone D (some samples in zone B). This fact shows that the exchange process was lesser than in aquifer qh for fresh water samples and the mixing towards enrichment of Na^+ prevails for saline water samples near the coastline. In the upper diamond, almost all samples are concentrated mainly in zone II, characterized for water types bicarbonate-chloride-sodium or chloride-bicarbonate-sodium and chloride-sodium. Meanwhile, a few samples fall in the zone I, characterized for water type bicarbonate-calcium and zone II, characterized for water type bicarbonate-sodium. These samples may be in locations with signs of desalinization due to mixing by directly receiving recharge from meteoric and surface water sources.

In Fig. 7, anions of aquifers qp₂₋₃ and n₂² are regularly distributed in zones E, B, and H. Water exchange was relatively strong during the transportation process from recharge to discharge areas, leading to an increase in chloride and sulfate contents at some places.

Cations of aquifer qp₂₋₃ are concentrated in zone D, where the exchange process towards the enrichment of Na^+ , Ca^{2+} , and Mg^{2+} simultaneously happened. The enrichment process of Ca^{2+} and Mg^{2+} only prevails in some samples in zone B. In the upper diamond, nearly all ultra-fresh water samples fall in zone II. The water transportation process was completed, so blackish water samples fall in the zone I, characterized for the predominance of the enrichment process of Ca^{2+} and Mg^{2+} (due to exchange-adsorption), and in zone II, characterized for the predominance of the enrichment

process of Na^+ and HCO_3^- (due to mixing with meteoric and surface water).

Meanwhile, cations of aquifer n_2^2 are not only concentrated in zone D, where the exchange process towards enrichment of Na^+ , Ca^{2+} , and Mg^{2+} simultaneously happened, but also many samples are concentrated in zone B showing the predominance of enrichment of Ca^{2+}

and Mg^{2+} . In the upper diamond, nearly all freshwater samples fall in zone I, characterized by the enrichment of Ca^{2+} and Mg^{2+} (due to exchange adsorption). The groundwater transportation process produces ultra-fresh and freshwater samples falling in zone III, characterized by the predominance of the enrichment process of Na^+ and HCO_3^- (due to mixing with meteoric and surface water).

Table 3. Statistical summaries of hydrogeochemical properties of porous aquifers

Property	Value	TDS	Na^+	Ca^{2+}	Mg^{2+}	Cl ⁻	HCO_3^-	SO_4^{2-}	Fe^{2+}	Fe^{3+}	NO_3^-
Aquifer qh	Min	35.3	0,1	1.0	0.1	3.6	-	-	-	-	-
	Max	38,403.0	10,958.2	465.9	1,541.3	21,092.8	604.1	3,218.0	1.4	5.8	141.8
	Average	5,765.5	1,537.2	85.2	209.1	2,952.9	122.0	427.3	0.1	0.2	11.2
	St deviation	12,374.3	3,442.0	134.3	451.7	6,755.7	122.2	912.5	0.2	0.6	24.9
Aquifer qp ₃	Min	31.4	1.6	-	-	7.1	-	-	-	-	0.02
	Max	38,282.0	10,290.6	1,578.2	1,292.0	20,029.3	628.5	2,343.9	2.6	13.1	25.6
	Average	2,503.6	615.6	55.3	82.8	1,204.4	71.8	162.4	0.2	0.6	3.5
	St deviation	8,396.7	2,118.9	205.8	277.7	4,176.5	108.1	513.4	0.5	2.4	6.4
Aquifer qp ₂₋₃	Min	31.4	1.6	-	-	7.1	-	-	-	-	-
	Max	38,282.0	10,290.6	1,578.2	1,292.0	20,029.3	628.5	2,343.9	2.6	13.1	25.6
	Ave	2,503.6	615.6	55.3	82.8	1,204.4	71.8	162.4	0.2	0.6	3.5
	SD	8,396.7	2,118.9	205.8	277.7	4,176.5	108.1	513.4	0.5	2.4	6.4
Aquifer n ₂ ²	Min	32.8	1.3	0.5	0.2	6.0	6.1	-	-	-	-
	Max	32,933.0	7,186.7	1,578.2	1,085.3	15,775.0	2,562.8	2,089.3	4.3	4.3	37.7
	Average	1,257.8	246.4	64.2	47.3	523.9	143.1	68.5	0.9	0.3	3.7
	St deviation	4,752.8	995.8	241.2	164.3	2,237.2	336.5	277.6	3.9	0.7	7.5

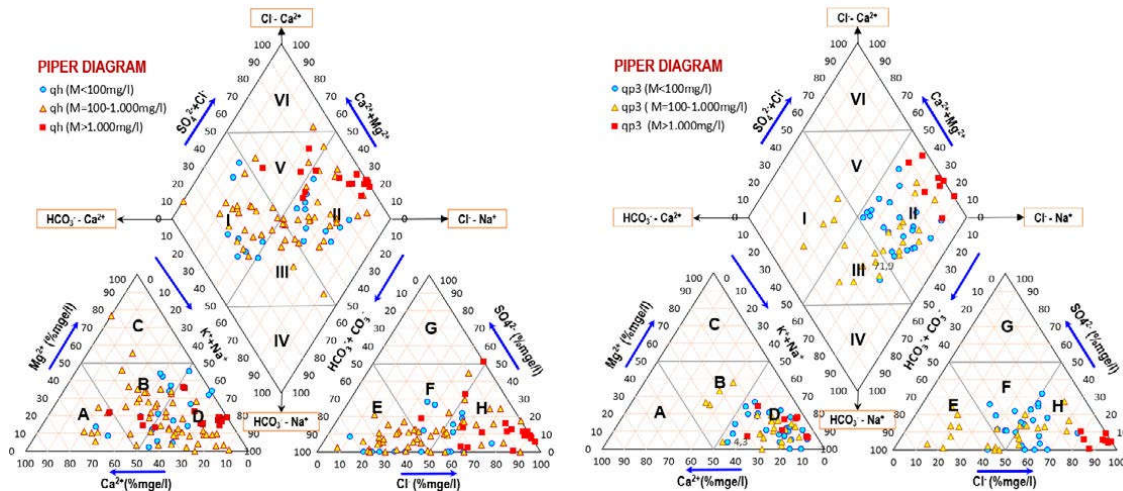


Figure 6: Piper diagram showing chemical composition of porous aquifers qh and qp₃

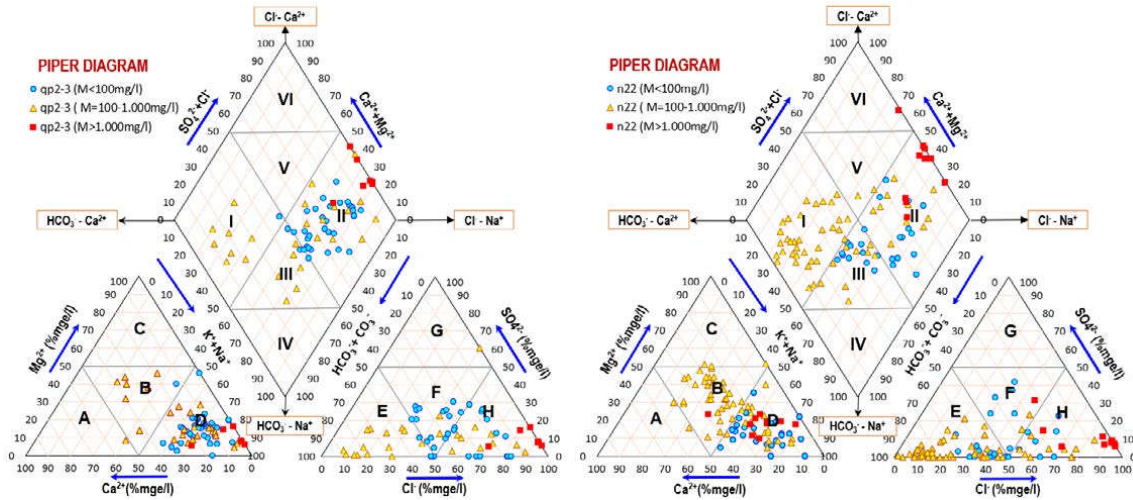


Figure 7: Piper diagram showing chemical composition of water in aquifers qp_{2-3} and n_2

In particular, many ultra-fresh, fresh, and saline water samples fall in zone II characterized by many processes, in which the trend of enrichment of Na^+ and Cl^- (due to the solution of salt in sediments of marine origin or mixing with current seawater). Particularly, samples with high TDS are possibly related to old buried seawater.

In short, the chemical composition of water in porous aquifers presents a nuanced formulation origin, reflecting the coexistence of various typical sources, including atmospheric- continental, continental, and marine influences (or those associated with present and paleo-seawater. In Gibbs diagrams, the

formulation origin of the main chemical composition is attributed to the interaction between soil rocks and water (Fig. 9 and Fig. 10). The role of meteoric and surface water (desalinization) is displayed in some samples. Some other samples in coastal areas show salinity intrusion. On Mercado diagrams (Fig. 8), the number of samples in the salinity-intruded area is significant, but in fact, saline water samples are few. Nearly all these samples are fresh water, even ultra-fresh (chloride content varies from 10 to 400 mg/l, with a ratio $rNa/rCl < 0.85$, possibly attributed to exchange-adsorption process inland that remarkably decreases Na^+ content (replaced by Ca^{2+} and Mg^{2+}).

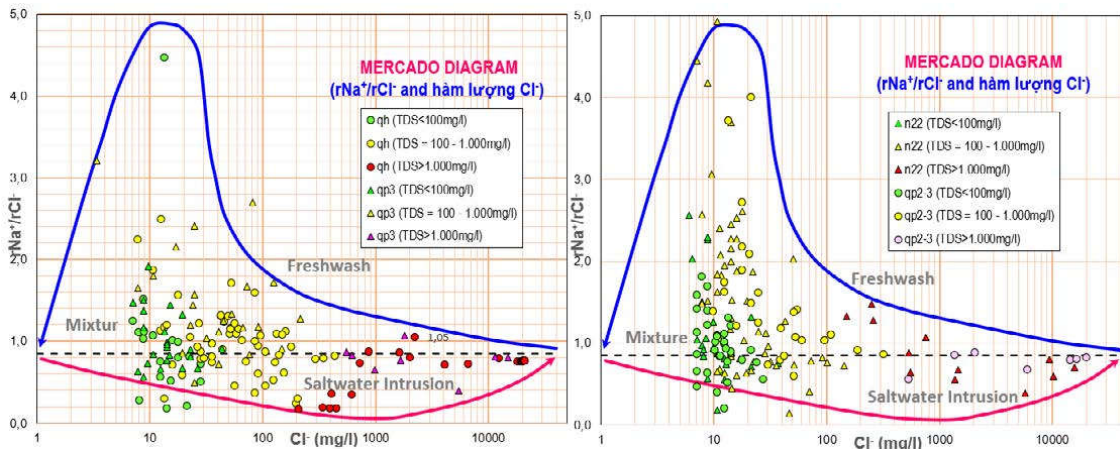


Figure 8: Chemical composition of the porous aquifer on Mercado diagrams

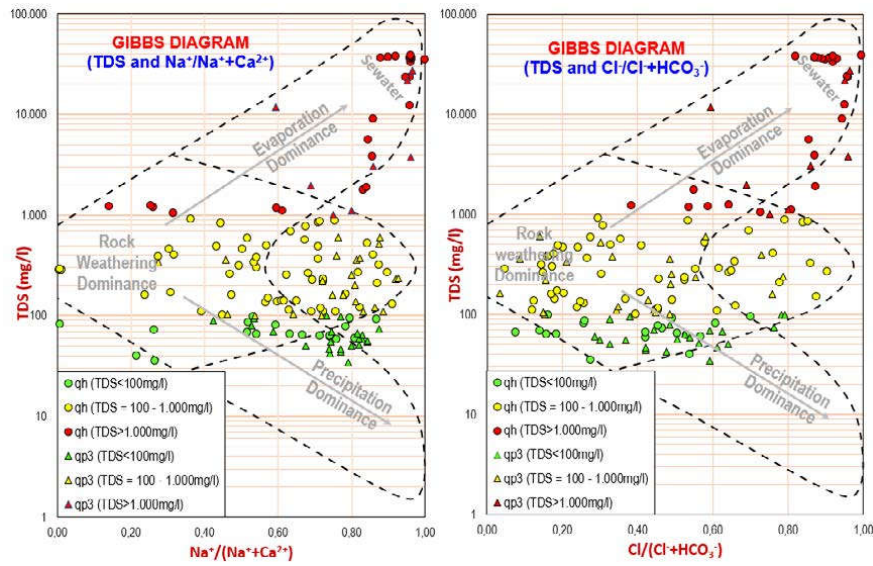


Figure 9: Chemical composition of porous aquifer qh and aquifer qp₃ on Gibbs diagrams

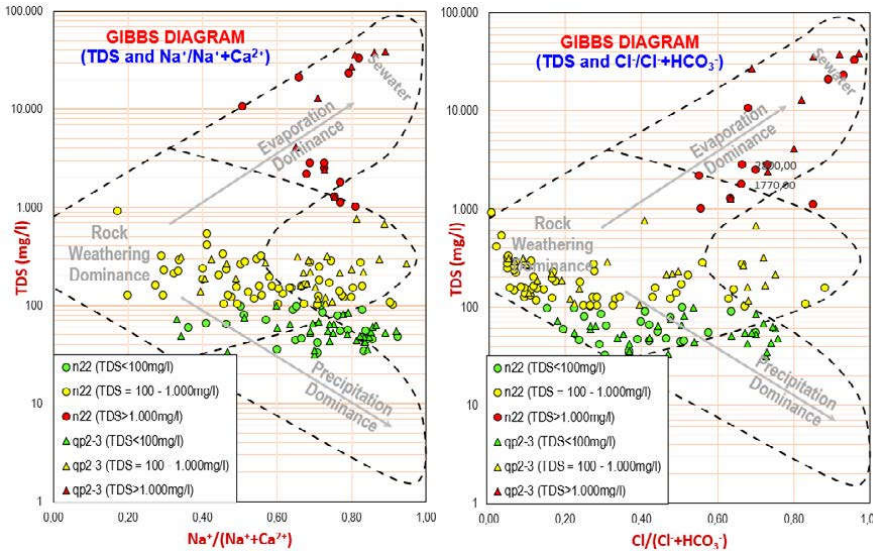


Figure 10: Chemical composition of porous aquifer qp₃ and aquifer n₂² on Gibbs diagrams

4. Conclusions

Based on the study results, we have drawn the following main conclusions:

- Fractured aquifers have mainly continental and atmospheric continental origins. Particularly, aquifer (ms) has changed its origin to marine in coastal areas. Meanwhile, porous aquifers have all typical atmospheric-continental, continental, and marine origins.

- Chemical compositions of groundwater were constituted from

combinations of processes. Depending on locations and aquifers, these process combinations change with different prevailing processes.

- The predominating processes for the whole province are exchange-adsorption, infiltration from meteoric water, and mixing fresh water from rivers. Thus, the resulting water types with low TDS (ultra-fresh and freshwater) have been observed, and distributed across most areas of the province.

- Areas with salinity intrusion occur primarily along the coast, stretching from Dat Do to the border with Binh Thuan province, as well as the estuaries of large rivers such as the Dinh and Thi Vai rivers. This is attributed to the advantageous mixing process involving current seawater and, in some cases, ancient buried seawater. In certain locations, signs of salinity intrusion were observed ($\text{TDS} < 1,000 \text{ mg/l}$) due to the solution-leaching process of salt in marine sediments, yet they have not been significantly affected by the mixing process with saline water.

The article provides information on the chemical composition of the main macro-elements in groundwater under natural conditions. With sufficient data on the chemical compositions of microelements, a more comprehensive assessment can be conducted, focusing particularly on the impact of pollution from human activities.

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