Formation and chemistry of the groundwater resource in the Mekong river delta, South Vietnam

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Abstract:

The origin and chemistry of the groundwater in the middle Pleistocene (qp_2^3), lower Pleistocene (qp_1), upper Pliocene (n_2^2), lower Pliocene (n_2^1), and the Miocene (n_1^3) in the Mekong river delta (MKRD) were investigated by using isotopic and geochemical techniques. The origin of the groundwater was evaluated based on the composition of the water stable isotopes (δ^2H and $\delta^{18}O$) in the local precipitation, in water from the rivers system, and in the groundwater samples. The hydraulic interaction between the surface water and the groundwater as well as between the aquifers was assessed by a statistical treatment for the mean and standard deviation of the $\delta^{18}O$ signature and based on the ^{14}C-ages of the water samples taken from different aquifers. The salinization of groundwater in the deep aquifers was investigated using the $\delta^{18}O$ signature combined with the geochemical composition of the water samples. It was revealed that the groundwater in the deep aquifers in the MKRD could be divided into two groups. The first group is fresh and represents the regional precipitation with the long traveling time ranging from older than 100 years to older than 40 ka BP (kilo years Before Present). The second group is the regional precipitation that is recharged from the remote areas mixed with the seawater. Statistical treatment with the mean $\delta^{18}O$ using the Mann-Whitney test showed that the water from the Mekong river system did not or very weakly recharged the deep aquifers. The groundwater in the deep aquifers in that region was likely to be connate, so that fresh groundwater resource in the region seemed to be limited. The chemistry of the groundwater in the study region is controlled by the incongruent dissolution of the Mg-calcite as well as sulfate and iron oxy-hydroxide reductions by organic matters presented in the aquifer sediment. The groundwater in the deep aquifers in the MKRD from some locations was saline, but the salinity in most aquifers was thought to result from the migration of saline water entrapped in the marine sediment pores to the fresh water in the aquifers. Meanwhile, in other locations, the salinity was suggested to result from the salt intrusion due to the over-abstraction rate, as it was evident from the $\delta^{18}O$ vs. [Cl^-] relationship, or due to the up conning of saline water from the deeper aquifers to the upper ones. Particular measures must be developed for the better management of groundwater in the MKRD to ensure a sustainable resource of freshwater being supplied to the local population in future.

Keywords: *groundwater ^{14}C-age, Mekong river delta, saline pore water migration, salt intrusion, Vietnam, water stable isotopic composition.*

Classification number: *4.2*

Introduction

Water is a vital natural resource for every nation. The life on Earth is possible only due to the existence of water on it. Although Vietnam is located in a tropical region, however, during the last decades, it has severely suffered from water shortage. During the dry season (from November till April), most of the reservoirs in the central part of the country were dried-up. Therefore, the farmers had to take their cattle far away from their villages for water. In the MKRD, the salt intrusion was observed very deep in the inland through the river system. The drinking water for the population in the MKRD is mostly abstracted from the groundwater sources. The demand for

clean water has steadily increased, leading to the abstraction yield of groundwater in the region to be higher year by year. At present, the rate of groundwater abstraction from the MKRD is around 2.10^6 m^3 a day [1].

There were two contrary hypotheses of groundwater resource formation in the MKRD. Based on the results of a study conducted during the 1980s, Nguyen Kim Cuong and his co-workers concluded that the artesian groundwater in the MKRD is of the paleo-type, having been closely buried since the Delta was formed, and that this water has no recharge [2]. However, Vu Van Nghi and Wesling [3] hypothesized that the origin of the groundwater in the MKRD was due to the

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local precipitation, and that groundwater in the region was continuously recharged from the surface sources at a very slow rate. Louvat and Ho Huu Dung [4] had conducted a study on the groundwater in the MKRD using water stable isotopes and dating the water by the radiocarbon method to determine the possible recharge areas for the aquifers in the region. Results of the study led them to the conclusion that the groundwater in the study area is recharged from areas at an altitude of around 170 m above the mean sea level. The recharge areas could be on the northeast highland, i.e. the Tay Nguyen plateau and/or the Cambodian territory [4].

The aim of this study is to investigate in detail the origin and salinization of water from the most important aquifers in the MKRD, based on the isotopic and chemical composition of different types of water, namely, local precipitation, river water, and groundwater. The use of the water stable isotopic content in conjunction with the water ionic content might help in the identification of processes, such as evaporation and salinization/desalination or mixing that affect the water bodies [5]. However, the use of radioactive isotopes of the minerals dissolved in water, e.g. ^{14}C in the total dissolved inorganic carbon (TDIC) could offer an idea about the movement direction of groundwater as well as the interaction between the aquifers in the study region [6].

Study area

The study was conducted in the MKRD and Fig. 1 depicts a map of the study region. The total area of the delta is around 54,250 km^2, in which around 31,650,000 habitants have settled, among whom, almost 65% are farmers [7].

Fig. 1. A map of the MKRD that comprises the Long An, Tien Giang, Dong Thap, Vinh Long, Ben Tre, Tra Vinh, Soc Trang, Hau Giang, Can Tho, An Giang, Kien Giang, Bac Lieu, and Ca Mau.

Geology of the region

The MKRD is one of the five geologic structural blocks that created the terrestrial Vietnam, namely, the northeast and northwest blocks in the northern part, Truong Son and Kon Tum blocks in the central part, and the Nam Bo block in the southernmost part. The Nam Bo block was covered with a very thick (> 6,000 m) sequence of Cenozoic formations that have de-formed and become basins for sedimentation [8, 9]. The Neogene and Upper Paleogene are the main deposits found in the Nam Bo geologic block that belong to the deltaic and marine sediment [8].

Hydrology of the region

The hydrologic regime of the MKRD is dominated by the Mekong river system that consists of the Tien (Mekong) river and the Hau (Bassac) river. These rivers systems are the chief contributors of freshwater to the region for irrigation. Annually, the Mekong river system discharges a total of about 500 billion cubic meters of freshwater through the Mekong river delta [10].

Complicating the natural stream system of the Mekong delta is a closely integrated man-made network of approximately 4,000 km of canals and inland waterways. These are subject to the tidal incursions of brackish water from Bien Dong, which might extend far inland during the dry season (February to April) on the Mekong river system.

Hydrogeology of the region

To date, eight aquifers in the MKRD have been identified as shown in Fig. 2 and Fig. 3 along transect northeast toward southwest, NE-SW (Binh Phuoc - Ca Mau) and transect west toward east, W-E (Dong Thap - Tra Vinh), respectively [11, 12]. The aquifers found are Holocene (qh), upper, middle, and lower Pleistocene symbolized, respectively, as qp_3, qp_2^3, and qp_1, upper Pliocene (n_2^2), lower Pliocene (n_2^1), Neogene (n_1^3), and bedrock (Mtz). From those aquifers, fresh water can be found only from the qp_2^3 and qp_1, n_2^2, n_2^1, n_1^3, Mtz, and occasionally in the qp_3 aquifers, but the Holocene aquifers contain either brackish or saline water that is not suitable for drinking purposes.
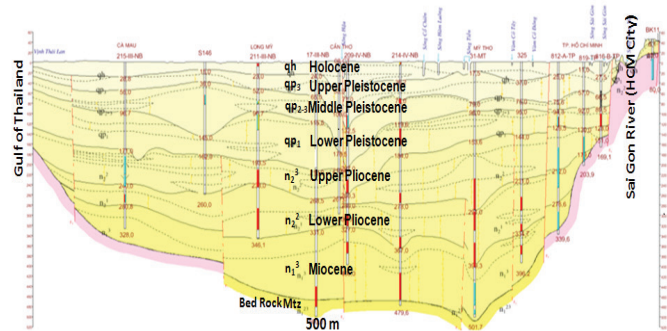

Fig. 2. The eight aquifers separated by the N-Q geologic structure along the transect NE-SW (Binh Phuoc - Ca Mau) in the MKRD [11, 12].
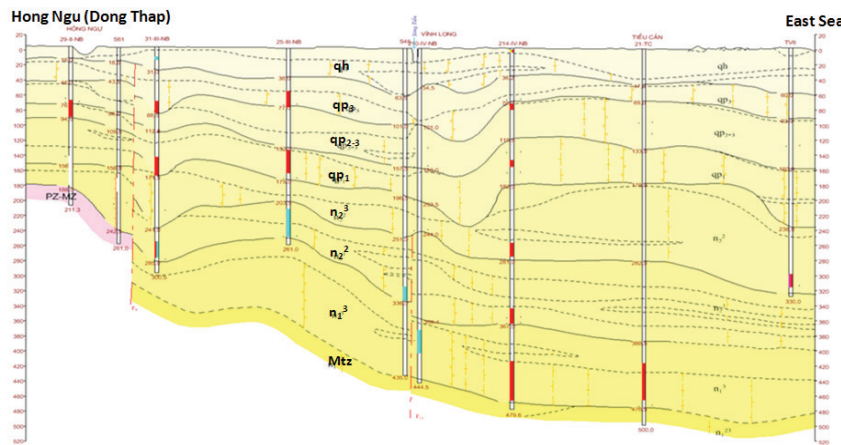
Fig. 3. The eight aquifers separated by the N-Q geologic structure along the transect W-E (Dong Thap - Tra Vinh) in the MKRD [11, 12].

The Holocene aquifers (qh) cover most of the plain with a thickness of up to 55 meters in the central part. The thickness of the upper Pleistocene aquifer (qp_3) is up to 33 m, from 50-55 m to 81 m on the land surface, following the middle Pleistocene (qp_2^3) of a thickness up to 141 m. Between the Holocene and the Pleistocene aquifers, there are aquitards of various thicknesses. All the Pleistocene aquifers are confined.

The upper and lower Pliocene aquifers (n_2^2, n_2^1) are confined, and their thickness is up to 100-145 and 90-120 m, respectively, in between the Tien and the Hau rivers, and in the Ca Mau peninsula. The fractured basement aquifer (Mtz) is confined and the groundwater is only tapped by a few boreholes in the Kien Giang province [12].

Sampling sites and sampling procedure

Groundwater was sampled from five aquifers as follows: qp_2^3, qp_1, n_2^2, n_2^1, and n_1^3. The samples were taken along two transects corresponding to the NE toward SW and W toward S as shown in Fig. 4 and Fig. 5.

To take groundwater samples, a sampling procedure recommended by the IAEA was implemented [13]. Briefly, it was as follows:

First, the stagnant water in the wells was completely flushed out by pumping out till the pH and the temperature of the water were unchanged. Alkalinity, including concentrations of bicarbonate ($[HCO_3^-]$), carbonate ($[CO_3^{2-}]$), and free carbon dioxide ($[CO_2]$), in the groundwater samples was then determined by titration using a HCl 0.1N solution. The content of total dissolved inorganic carbon (TDIC) in the samples was calculated by summing up the concentrations of $[HCO_3^-]$, $[CO_3^{2-}]$, and $[CO_2]$ [14].

The TDIC in the groundwater used to determine the content of carbon-13 and carbon-14 needed for the radiocarbon dating was precipitated in the form of $BaCO_3$ at pH = 10 by using a saturated $BaCl_2$ solution, following a procedure described in [13].

Rain water was collected monthly using a device constructed following an IAEA recommendation [15]. The device was installed on the roof of the premises of the Center for Nuclear Techniques in Ho Chi Minh (HCM) city. The surface water was sampled at a depth of 0.5 m from the surface and around 1 m from the bank of the Tien and Hau rivers.

For chemical analyses, around 100 ml of groundwater samples were first filtered through 0.45 mm mesh filters to remove the suspended matters and then they were split into two parts. One part was acidified with 2-3 drops of HNO_3 (65%, PA grade, Merck, Germany) to make pH of the samples 1-2. These samples were subjected to analysis for cations, whereas the other part was kept without acidification for anion analysis.

For the tritium determination, one liter of water was sampled into a HDPE bottle with a tight cap to avoid isotopic
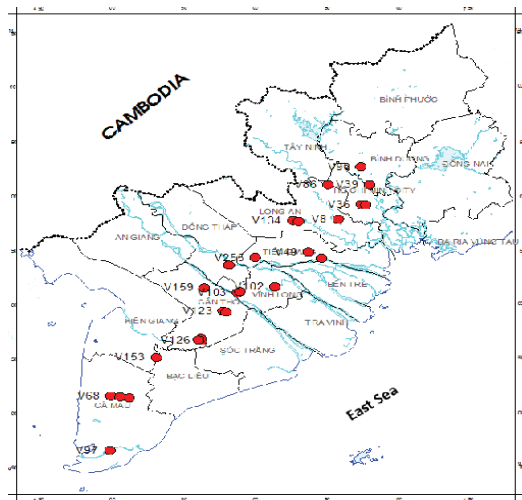

Fig. 4. Sampling locations along the transect NE toward SW (Binh Phuoc - Ca Mau).

Fig. 5. Sampling locations along the transect W toward E (Dong Thap - Tra Vinh).

exchange with the atmospheric moisture. The samples were transferred to the laboratory in Hanoi for further treatment and measurement for tritium activity.

Sample treatment and analytical procedure

The ionic content of the water samples was quantified by ion chromatography using a DIONEX 600 from the Institute for Nuclear Science and Technology (INST in Hanoi). Stable isotopes (^{2}H, ^{18}O, and ^{13}C) were analyzed at the INST with an Isotope Ratio Mass-Spectrometer (IR MS, MicroMass, JV, UK), equipped with an Elemental Analyzer (Eurovector, Italy). To determine the deuterium composition, the samples were pyrolyzed on a Ni catalyst at 1,050°C to form hydrogen, followed by the purification on a chromatographic column before entering the ion source of the IS MS. The water oxygen was first converted into CO_2 gas by decomposing the water samples on glassy carbon at 1,250°C. The formed CO_2 was subjected to a chromatographic purification before entering the ion source of the IR MS.

Upon the arrival at the laboratory, the barium carbonates were carefully washed off with hot deionized water to remove the alkaline excesses and then dried under a vacuum. The dried carbonate samples with an amount of around 100 mg were then wrapped in tin capsules and subjected to decomposition at 1,250°C with a CuO_2 catalyst in the Elemental Analyzer. The formed CO_2 was then allowed to pass through a chromatographic column to remove any contamination before entering the ion source of the IR MS to determine the carbon-13 content. The water stable isotopic composition and carbon-13 content in TDIC were expressed in the delta notation (δ) as follows:

$$\delta^2 H = (\frac{R_{2H, sample}}{R_{2H, std}} - 1).1000 \tag{1}$$

$$\delta^{18} O = (\frac{R_{18O, sample}}{R_{18O, std}} - 1).1000 \tag{2}$$

$$\delta^{13} C = (\frac{R_{13C, sample}}{R_{13C, std}} - 1).1000 \tag{3}$$

where: $R_{2H, sample}$, $R_{2H, std}$, $R_{18O, sample}$, $R_{18O, std}$, $R_{13C, sample}$ and $R_{13C, std}$ are the isotopic ratios of ^{2}H/^{1}H, ^{18}O/^{16}O, and ^{13}C/^{12}C samples and standards, respectively. The value of the delta notation is expressed in per mil (‰). The standard used in the analyses of the water stable isotopes is the Vienna Standard of Mean Ocean Water (VSMOW), but that for ^{13}C in TDIC is the Vienna Pee Dee Belemnite (VPDB) [16].

The precision of δ^2H was ±2‰, and that of δ^{18}O and δ^{13}C was ±0.2‰. A quality assurance and quality control program was applied for the ionic content determination by analyzing the standard solutions supplied by the IC supplier (DIONEX). The standard deviation of the analytical results was more than ±3% from the certified value for a respective constituent.

For the tritium dating, the water samples were first subjected to distillation to remove the minerals dissolved until the electric conductivity was less than 10 μS cm^{-1}. Around 500 ml of the distilled water samples were then subjected to the electrolytic enrichment for tritium at 4°C till around 10 ml was attained [17, 18]. The tritium-enriched water samples were purified again by distillation and then mixed with low-tritium Ultimagold scintillation cocktail (Hewlett-Packard, HP Supplier) in vials of 20 ml capacity for counting the ^{3}H activity on a low background HP Liquid Scintillation Counter TriCarb TR 3770. The ^{3}H activity in the water samples was expressed in the Tritium Unit (TU, 1 TU = 0.118 Bq L^{-1}). The limit of detection for ^{3}H by the procedure was estimated to be as low as 0.4 TU. The accuracy of the determination was checked by the participation in the inter-comparison exercises organized by the IAEA Isotope Hydrology Section in the years 2004 and 2008 [19, 20]. In the 2004 exercise, the Hanoi laboratory (No.74) produced results having Z-scores of -1.25 and 0.59 for the samples of 1.74 TU and 5.43 TU, respectively. In the 2008 exercise, the laboratory (No.27) produced results with Z-scores of 0.42 and 1.57 for the samples of 4.07 TU and 1.54 TU, respectively.

The carbon-14 activity in the TDIC used for dating the groundwater samples was measured in the Center for Nuclear techniques in HCM city. It was there that the $BaCO_3$ was first converted into CO_2 by decomposing it with concentrated H_3PO_4 (PA grade, Merck supplier), followed by the benzene synthesis [21]. The benzene obtained was mixed with the Ultimagold scintillation cocktail (HP Supplier) and then counted for the ^{14}C activity on the HP LSC TriCarb TR 3770. The ^{14}C content in the samples was expressed in percent of the modern carbon (pMC). This is a relative measurement of the ^{14}C activity in the samples and those in a standard supplied by the National Institute of Standards and Technology (NIST, USA). The ^{14}C NIST standard used in this study was oxalic acid II (ox-II) made from the molasses of French beet planted in 1977, which has a ^{14}C activity of 0.2147 Bq/g C and δ^{13}C = -25‰ [22].

Groundwater transit time (the age) estimation

The age of the groundwater is defined as the transit time between the infiltration zone and the discharge point [5]. The aim of the age determination is to evaluate the flow direction of water in an aquifer. The groundwater age calculation was made based on the data of ^{14}C activity and d^{13}C in the TDIC. The principle of the ^{14}C-dating method was the law of radioactive decay, and in the case of dating the groundwater, it was expressed by Equation (4).

$$^{14}t = 8268\ln \frac{^{14}a_{in}^0}{^{14}a_{sample}} (a\ BP) \tag{4}$$

where: ^{14}t denotes the age, in years Before Present (BP), of a groundwater sample estimated by the ^{14}C activity in TDIC; the number 8268 is the quotient of the half-life of the ^{14}C-isotope

(5,730 a) to ln2; $^{14}a_{in}^{0}$ is the relative initial content of ^{14}C in TDIC before entering the saturated zone in pMC; and $^{14}a_{sample}$ is the relative ^{14}C content in pMC in TDIC of the sample.

The estimation of the age of groundwater by the Eq. 4 requires corrections for the $^{14}a_{in}^{0}$, because before entering the saturated zone, the carbon in the bicarbonate would participate in the isotopic exchange with the carbon in the biogenic CO_2 that would be released from the plant root respiration on one hand, and, on the other hand, a new portion of bicarbonate could be formed there due to the oxidation of organic matters or the dissolution of the inorganic carbonates presented in the unsaturated zone. All these processes could modify the value of $^{14}a_{in}^{0}$. To do the correction, an isotope mixing model referred to as complete exchange with CO_2 in the unsaturated zone was proposed by Gonfiantini [23] for a closed system and was applied as follows:

$$^{14}a_{in}^{0} = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{cc}}{\delta^{13}C_{CO_{2,org}} - \delta^{13}C_{cc} + \varepsilon_{CO_2/DIC}} \quad (5)$$

where: $\delta^{13}C_{DIC}$, $\delta^{13}C_{cc}$, and $\delta^{13}C_{org}$ are the content of carbon-13, respectively, in TDIC in a water sample, in calcareous materials, and in the biogenic carbon dioxide that originates from the decomposition of organic matters; $\varepsilon_{cc/DC}$ is the fractionation coefficient for ^{13}C in the isotopic exchange reaction between carbon dioxide and TDIC and is temperature dependent [24].

$$\varepsilon_{CO_2/DIC} = \left(-\frac{9483}{T} + 23.89\right) ‰ \quad (6)$$

where: T is the temperature of water sample in Kelvin.

In the study area, the $\delta^{13}C_{cc}$ was found to be ranging from 1‰ to 2‰, and the average value of 1.5‰ was taken in the correction for $^{14}a_{in}^{0}$. The $\delta^{13}C_{CO_{2,org}}$ in Equation (5) was taken as high as -23‰, as it was characterized by the carbon dioxide generated from the C3 plants in the tropical areas. Details for the procedure of $^{14}a_{in}^{0}$ calculation can be found in Fontes [25]. The data of the ^3H activity were used just to confirm whether the studied water sample was old or modern.

Statistical treatment of isotopic data

To get an original isotopic signal, samples having water stable isotope data disturbed by evaporation or by mixing with seawater were eliminated. The mean of $\delta^{18}O$ and its standard deviation were calculated for each group of samples, i.e. for the river's water and groundwater from each aquifer qp_2^3, qp_2^1, n_2^2, n_2^1, and n_1^3.

To compare the means of the groups, a non-parametric test, namely, the Mann-Whitney test, which allows the comparison of independent series of different size without any preliminary hypothesis was used. In our case, the sample size was large enough to consider that the variable built from the test, z, would follow a normal distribution. Therefore, the difference of means between the groups would be significant, if z>1.96 (critical value at a 5% limit), and very significant, if z>2.58 (critical value at a 1% limit).

Results

The isotopic composition of deuterium (δ^2H), oxygen-18 ($\delta^{18}O$) as well as the tritium concentration in water, and the composition of carbon-13 ($\delta^{13}C$) and the content of carbon-14 in TDIC are presented in Table 1 along with the sampling locations. The content of the major ionic constituents dissolved in water are presented in Table 2.

Table 1. Sampling locations, water isotopic compositions and ^{14}C-age of ground-water from different aquifers in the MKRD.

Middle Pleistocene aquifer (qp_2^3), Transect NE-SW: HCM-Ca Mau								
Sample code	**Co-ordinate**		**Depth, m**	**$\delta^{18}O$, ‰**	**δ^2H, ‰**	**^3H, TU**	**$\delta^{13}C$ (TDIC), ‰**	**^{14}C(TDIC), pMC**	**Age (TDIC), years**
	X	**Y**							
V36	18676015	1193936	40	−6.2	−39.8	0.4	−24.4	73 ± 0.3	132 ± 20
V99	18495854	968776	130	−6.4	−44.8	−<LOD*	−15.6	1.3 ± 0.5	34 900 ± 4 100
V126	18564782	1068665	117	−6.4	−44.5	−<LOD	−12.0	9.3 ± 0.2	16 700 ± 1 200
Middle Pleistocene aquifer (qp_2^3), Transect W-E: Dong Thap-Tra Vinh									
V54	18661369	1065168	108	−6.7	−45.2	−<LOD	−14.4	10.4 ± 0.5	17 200 ± 1 500
V76	18575206	1115425	95	−4.4	−37	−<LOD	−14.8	12.2 ± 0.5	16 200 ± 1 800
V115	18517297	1187001	50	−6.0	−40.1	−<LOD	−6.2	26.6 ± 08	3 200 ± 300
V178	18561605	1180746	78	−6.3	−40.5	−<LOD	−5.8	23.6 ± 0.9	4 000 ± 400
Lower Pleistocene (qp_1), Transect NE-SW (HCM-Ca Mau)									
Sample code	**Co-ordinate**		**Depth, m**	**$\delta^{18}O$, ‰**	**δ^2H, ‰**	**^3H, TU**	**$\delta^{13}C$(TDIC), ‰**	**^{14}C(TDIC), pMC**	**Age (TDIC), years**
	X	**Y**							
V39	18681757	1212154	100	−7.3	−48.4	−<LOD	−23.3	73.0 ± 1.6	2 600 ± 300
V152	18530684	1054018	132	−6.2	−41.6	−<LOD	−15.9	7.6 ± 0.4	20 700 ± 2 300
V155	18533505	1076938	210	−6.2	−41.6	<LOD	−15.7	17.6 ± 0.7	11 400 ± 1 100
Lower Pleistocene (qp_1), Transect W-E: Dong Thap-Tra Vinh									
V77	18577871	1115588	98	−6.2	−44.1	−<LOD	−15.0	16.9 ± 0.6	13 500 ± 900

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V172	18517452	1187175	161			−<LOD	−10.8	16.0 ± 0.7	13 900 ± 600
V176	18613774	1122479	371			−<LOD	−7.6	6.1 ± 0.6	21 000 ± 2 100
V278	18620457	1111142	165	−5.5	−42.4	−<LOD			

Upper Pliocene aquifer (n_2^2), Transect NE-SW: HCM-Ca Mau

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V9	18653687	1169165.9	195	−7.2	−47.1	−<LOD	−21.1	11.5 ± 0.7	17 900 ± 1 400
V102	18615632	1118071	267	−4.9	−35.5	−<LOD	−8.9	20.2 ± 0.2	12 900 ± 1 200
V153	18533043	1053242	210	−6.4	−43.1	−<LOD	−12.9	3.4 ± 0.2	25 600 ± 2 100
V159	18566657	1117305	220	−5.5	−43.7	−<LOD	−15.4	19.9 ± 0.5	12 400 ± 1 200

Upper Pliocene aquifer (n_2^2), Transect W-E: Dong Thap-Tra Vinh

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V105	18522010	1185978.5	103	−5.8	−42.3	−<LOD	−10.8	22,6 ± 0,3	7 200 ± 700
V108	18646466	1118006	261	−2.0	−13.7	-	-	-	-
V179	18561605	1180746	323	−7.4		<LOD	−8.5	9,8 ± 0,9	17 000 ± 2 200

Lower Pliocene (n_1^1), Transect NE-SW: HCM-Ca Mau

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V31	18684831	1194150	100	−7.6		−<LOD	−19.8	16.9 ± 0.4	15 900 ± 1 000
V35	18679045	1193786	200	−7.7	−52.4	−<LOD	−19.6	17.3 ± 0.4	15 400 ± 1 000
V101	18621408	1114813	442	−2.42	−17.4	-	−6.3	-	-
V247	18565590	1115374	295	−7.0	−49.0	−<LOD	−14.5	3.0 ± 0.4	27 400 ± 2 400

Lower Pliocene (n_1^1), Transect W-E: Dong Thap-Tra Vinh

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V104	18588283	1112838	366	−6.3	−42.0	−<LOD	−9.0	0.9 ± 0.2	33 500 ± 2 600
V111	18583755	1138106	390	−7.3	−51.1	−<LOD	−9.6	2.7 ± 0.7	24 600 ± 2 300
V122	18581619	1094903	462	−6.2	−42.4	<LOD	−8.0	2.1 ± 0.2	25 400 ± 2 700

Neogene aquifer (n_1^3), Transect NE-SE: HCM-Ca Mau

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V88	18500617	967772	360	−6.9	−40.8	−<LOD	−11.9	4.1 ± 0.4	22 800 ± 2 200
V104	18591545	1113733	366	−6.3	−42.0	−<LOD	−9.0	0.9 ± 0.2	33 500 ± 3 500
V111	18583755	1138106	390	−7.3	−51.1	−<LOD	−9.6	2.7 ± 0.7	24 600 ± 2 300
V255	18602094	1145026.4	360	−7.6	−57.3	−<LOD		10.5 ± 4.8	18 700 ± 1 800

Neogene aquifer (n_1^3), Transect W-E: Dong Thap-Tra Vinh

Sample code	Co-ordinate X	Y	Depth, m	$\delta^{18}O$, ‰	δ^2H, ‰	^3H, TU	$\delta^{13}C$(TDIC), ‰	^{14}C(TDIC), pMC	Age (TDIC), years
V104	18591545	1113733	366	−6.3	−42.0	−<LOD	−9.0	0.9 ± 0.2	33 500 ± 3 500
V106	18577373	1136181	364	−6.7	−47.7	−<LOD	−7.3	6.2 ± 0.4	15 800 ± 1 000
V111	18583755	1138106	390	−7.3	−51.1	−<LOD	−9.6	2.7 ± 0.7	24 600 ± 2 400
V112	18574141	1138185	318	−6.8	−47.1	−<LOD	−7.9	13.6 ± 0.4	10 100 ± 1 000

*LOD of ^3H was 0.4 TU.

Table 2. Hydrogeochemical composition of groundwater in the MKRD.

Middle Pleistocene aquifer (pq_2^3)

Sample code	T, ˚C	pH	EC, mS cm⁻¹	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V36	29.5	4.6	66		0.02	0.35		0.18	0.35	0.20		
V54	29.5	6.9	860	1.88	0.22	2.31	3.00	3.09	0.72	7.10		0.69
V76	28.0	6.8	1030	2.47	0.73	4.55	2.70	3.70	4.79	5.04	1.48	0.40
V115	29.0	6.5	2268	0.59	0.61	14.14	3.15	4.70	18.30	7.20		
V126	29.0	6.0	950	0.73	0.31	5.96	1.25	1.85	2.05	6.92		1.81

Lower Pleistocene aquifer (pq_1)

Sample code	T, ˚C	pH	EC, mS cm⁻¹	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V39	31.0	5.7	115		0.02	0.73	0.20	0.29	0.44	0.56		0.11
V72	31.0	7.4	1300	1.03	0.36	9.78	0.96	1.89	4.09	8.08	0.32	0.14
V278	28.5	6.5	593			5.83				7.28		

Upper Pliocene aquifer (n_2^2)

Sample code	T, ˚C	pH	EC, mS cm⁻¹	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V8	31.5	6.5	1330	2.10	0.35	5.74	5	2.36	10.59	2.56		0.12
V42	28.5	4.6	139		0.06	1.03	0.08	0.25	0.10	1.34		

Sample code	T, °C	pH	EC, mS cm^{-1}	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V70	35	7.4	1246	1.14	0.21	9.7	1.16	1.24	2.45	8.28	1.12	0.45
V71	36	7.8	1127		0.68	8.74	0.76	1.40	1.80	8.36	0.80	0.43
V98	36	8.2	2190	0.55	0.11	20.12	0.60	1.23	6.23	11.08	1.52	3.00
V125	30	7.9	752	0.14	3.80	255.65	24.80	52.65	312.56	11.52		12.45
V143	28.5	7.3	650		0.10	3.95	1.12	1.24	3.09	3.38		
Lower Pliocene aquifer (n_2^1)												
Sample code	T, °C	pH	EC, mS cm^{-1}	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V35	33	6.1	233	4.78	0.15	0.81	0.72	0.66	0.21	1.92		0.26
V95	28	6.8	380	0.14	0.16	0.60	1.84	1.10	0.20	3.46		0.3
V102	31	7.8	33500	0.21	4.41	234.16	33.07	63.06	318.55	3.40		12.79
V108	29	6.5	35570	2.46	12.79	343.63	25.75	86.25	428.5	3.32		36.4
V113	29	8.4	977		1.05	8.09	0.25	0.35	2.50	5.60	0.60	1.02
Neogene aquifer (n_1^3)												
Sample code	T, °C	pH	EC, mS cm^{-1}	CO_2	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
V88	38	8.1	760	0.27	0.12	7.25	0.4	0.17	0.75	6.60		0.23
V101	27	8.4	33587		1.67	358.18	3.82	2.31	356.96	6.04	0.20	2.38
V104	35	8.4	2730	0.50	0.26	23.88	1.38	1.67	18.12	6.79	0.40	1.96
V106	31	8.7	1910	0.41	0.51	16.87	1.00	0.58	5.50	6.50	0.80	6.28
V111	39	7.2	1120	0.30	0.10	10.54	0.55	0.32	3.91	7.44		0.31
V112	29	8.4	1250		0.17	11.22	0.76	0.82	3.52	7.52	1.20	0.68

Unit: meq L^{-1}.

Figure 6 depicts the regional meteoric water line (RMWL) determined in HCM and the water line for the Tien and Hau rivers. The RMWL in HCM could be considered to represent the whole MKRD, as the city is located at an elevation comparable to the average elevation of the region. The RMWL follows a model described by an expression as follows:

$$\delta^2H = 7.37\delta^{18}O + 5.15 \qquad (R^2 = 0.966) \qquad (7)$$

The isotopic composition of water from the Tien and Hau rivers did not differ from each other in the Mann-Whitney test at a 5% limit, and a model of the water line for the two rivers was as follows:

$$\delta^2H = 6.57\delta^{18}O - 3.36 \qquad (R^2 = 0.875) \qquad (8)$$

The slope of the water line for the rivers is lower than those for the RMWL in HCM (Eqs. 7 and 8), reflecting the
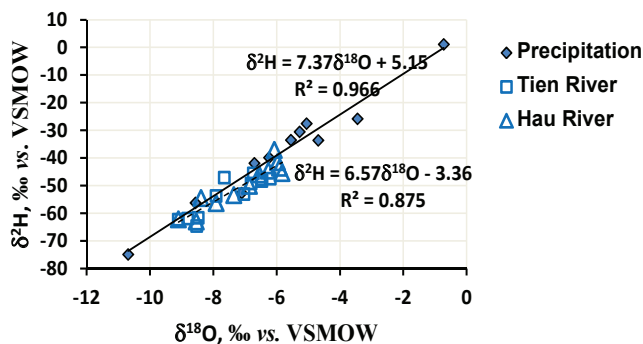
evaporative effect of the surface waters [5]. The RMWL in HCM is similar to that in Bangkok (Thailand) that was $\delta^2H = (7.35 \pm 0.08) \delta^{18}O + (5.33 \pm 0.50)$ ($R^2 = 0.96$) [26]. This is due to the fact that HCM city and Bangkok are located almost at the same latitude and at the same elevation and the mean annual air temperature in the two cities is in the same range of $(28\text{-}30)^0C$.
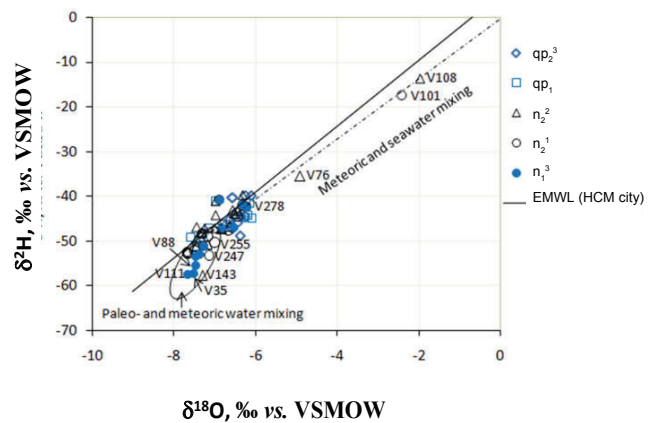

Fig. 7. Isotopic composition of groundwater in the deep aquifers of the MKRD along with the Regional Meteoric Water Line (RMWL, HCM city).

Figure 7 depicts the water line for groundwater from five aquifers as follows: qp_2^3, qp_1, n_2^2, n_2^1, and n_1^3 throughout the MKRD and sampled along the two transects.

Fig. 6. Regional meteoric water line (RMWL) for HCM city and the water line for the Tien and Hau rivers in the Mekong river delta.

Discussion

The age of groundwater from the five aquifers, namely,

middle Pleistocene ($qp_2{}^3$), lower Pleistocene (qp_1), upper Pliocene ($n_2{}^2$), lower Pliocene ($n_2{}^1$), and the Miocene ($n_1{}^3$) in the MKRD was older than 100 years as the tritium content in groundwater taken from these aquifers was found to be lower than the LOD of 0.4 TU of the analytical procedure. In the precipitation collected in HCM and water from the Tien and Hau rivers, the ^{3}H content ranges from 0.6 to 3.5 TU (Table 1). This reflects the fact, that at present, the bomb tritium has already gone to the southern hemisphere, and the radioactive isotope of hydrogen in surface water in the region is mainly derived from the nuclear reactions in the atmosphere [27]. Unfortunately, in this study, no isotopic data for the Holocene (qh) and upper Pleistocene aquifers (qp_3) were available, so there is no idea about the hydraulic interaction of surface water with the water in the shallow aquifers. The water's isotopic composition can be used to judge whether the water from the two adjacent aquifers, e.g. surface water and water in aquifer $qp_2{}^3$ or water in aquifers $qp_2{}^3$ and qp_1 etc., do interact with each other hydraulically by performing the Mann-Whitney statistical test on the mean difference, based on the mean $\delta^{18}O$ or δ^2H and its standard deviation [4]. Table 3 shows the results of the test using the mean $\delta^{18}O$ for each pair of the aquifers along transects.

As seen from Table 3, in the Mekong river delta, the water from the Tien and Hau rivers (transect W-E, Fig. 5) did not interact hydraulically with those in the middle Pleistocene

($qp_2{}^3$) aquifer, as the mean $\delta^{18}O$ in water from the rivers and the $qp_2{}^3$ aquifer was very significantly different from each other (z-value was 2.81 higher than the critical values of 2.58 at $\alpha = 1\%$, Table 3). In other words, the rivers do not recharge their water to the $qp_2{}^3$ aquifer, which also implies that the rivers do not recharge their water to deeper aquifers as well. Along the transect NE-SW (Fig. 4), it appears that all the studied aquifers were hydraulically connected with each other, as the mean $\delta^{18}O$ in the water of adjacent aquifers was insignificantly different from each other (z-value was lower than the critical value of 1.96 at $\alpha = 5\%$, Table 3).

In the study of Louvat and Ho Huu Dung [4], it was found that in the MKRD, there was no hydraulic connection between the pairs of adjacent aquifers. Probably, this was true for a time when the freshwater abstraction from those aquifers was not so intense like today. A recent survey showed that in the MKRD, at present, each day around 1,230,000 m³ of groundwater is being abstracted, mainly, from the Pleistocene and Pliocene aquifers that were more than 240% of those freshwater production yield (510,761 m³ day⁻¹) before 1990 [28]. It seems that the heavy freshwater mining in the region today has caused depression of the water table in the production aquifers, leading to inter-aquifer leakages, and as a result, the mixing of water from the upper aquifer with those in the lower aquifer has occurred. The inter-aquifer leakage has been observed in the Great Artesian basin in Australia and in the Canterbury plain in New Zealand

Table 3. The Mann-Whitney statistical treatment for the means $\delta^{18}O$ and its standard deviation to show the hydraulic interaction between the adjacent aquifers in the MKRD region.

Z-test of two sample for means					
Water group	**$\delta^{18}O$ mean, ‰ vs. VSMOW**	**Standard error, ($\pm$)**	**Comparison**	**Value of z ($\alpha = 0.05$)**	**Difference between means**
NE-SW Transect (Fig. 4)					
$qp_2{}^3$	-6.38	0.68			
qp_1	-6.75	0.76	$qp_2{}^3$-qp_1	1.04	no
$n_2{}^2$	-6.70	0.65	qp_1-$n_2{}^2$	-0.12	no
$n_2{}^1$	-7.07	0.51	$n_2{}^2$-$n_2{}^1$	0.79	no
$n_1{}^3$	-6.87	0.61	$n_2{}^1$-$n_1{}^3$	0.76	no
W-E Transect (Fig. 5)					
Rivers	-7.29	1.10			
$qp_2{}^3$	-6.46	0.16	Rivers-$qp_2{}^3$	-2.81($\alpha = 0.01$)	very significant
qp_1	-5.91	0.33	$qp_2{}^3$-qp_1	-1.05	no
$n_2{}^2$	-7.44	0.75	qp_1-$n_2{}^2$	2.66($\alpha = 001$)	very significant
$n_2{}^1$	-7.20	0.25	$n_2{}^2$-$n_2{}^1$	-0.42	no
$n_1{}^3$	-6.74	0.41	$n_2{}^1$-$n_1{}^3$	-1.07	no

[29, 30]. Inter-aquifer leakage in the MKRD could happen, as there the sediment primarily comprised the fluvial-marine type with high coarse sand content, making the conductivity high. Apparently, the inter-aquifer leakage has caused the water in the Pleistocene and the Pliocene aquifers in the Mekong river delta to mix with each other so that the isotopic composition of water in the two aquifers is insignificantly different from each other (transects NE-SW and W-E, Table 3).

As seen from Fig. 7, the groundwater in the deep (qp_1, n_2^2, n_2^1, and n_1^3) aquifers in the MKRD displays a mixing of three water types, namely, paleo-water, regional meteoric water, and seawater. The mixing feature of the paleo-water with meteoric and seawater as depicted in Fig. 7 was similar to those characterized for groundwater in the Qatar city [31]. The Mann-Whitney statistical test showed that the mean of $\delta^{18}O$ in the recent precipitation during the rainy season was significantly different from that in the groundwater taken along the W-E transect (Fig. 5). This means that the recent local meteoric water does not recharge the deep aquifers in the MKRD. From the data of stable isotopic composition and ^{14}C-ages (Table 1), it was thought that the groundwater in the deep aquifers of the MKRD was connate like those in the suggestion made by Nguyen Kim Cuong, et al. [2], or it was recharged from the remote areas at a slow speed.

The chloride concentration in most of the groundwater samples from different aquifers in the MKRD was lined up along a horizontal line in the graph of $\delta^{18}O$ *vs.* [Cl^-] with a mean $\delta^{18}O$ around -7‰ as shown in the Figs. 8 and 9 for the transects NE-SW and W-E, respectively. The data that were taken to draw the Figs. 8 and 9 were from the Tables 1 and 2. In Figs. 8 and 9, the horizontal line characterizes the migration or diffusion of the saline water entrapped in the sediment pores into the fresh water present in the aquifer, whereas the doted arrows (Figs. 8 and 9) characterize the salt intrusion [6, 32]. This result is consistent with those derived from the δ^2H *vs.* $\delta^{18}O$ relationship (Fig. 7) that was discussed above.

The salt intrusion and saline pores' water migration from the aquifer sediment (Figs. 8 and 9) resulted in a mixture of the freshwater and saline water, as it is evident from Figs. 10A and 10B, respectively, for the qp_2^3, qp_1, and n_2^1, n_2^2 along the transect NE-SW (Fig. 4) as an example for the entire MKRD region.

Fig. 8. Scatter plot of $\delta^{18}O$ *vs.* chloride concentration ([Cl^-]) in groundwater from the MKRD along transects NE-SW (Fig. 4). The concentration of chloride ion was expressed in the logarithmic scale.
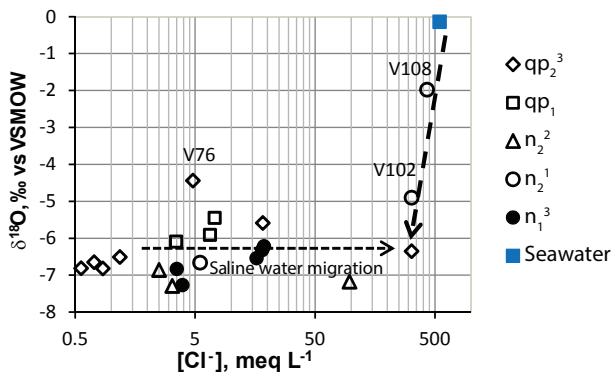
Fig. 9. Scatter plot of $\delta^{18}O$ vs. chloride concentration ([Cl^-]) in the groundwater in the MKRD along transect W-E (Fig. 5). The chloride concentration was expressed in the logarithmic scale.
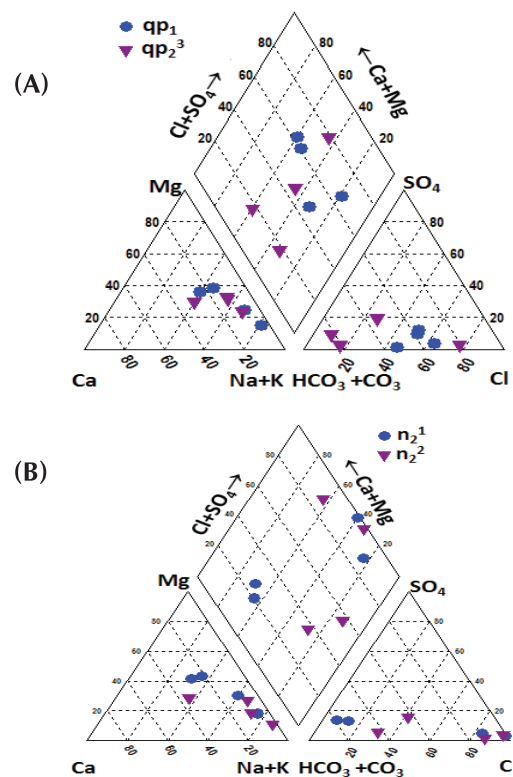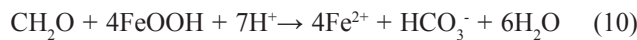

Fig. 10. Piper diagrams are showing the mixing of saline pore water with fresh water in the qp_2^3 and qp_1 (A) and seawater with freshwater in the n_2^1 and n_2^2 (B) along the NE-SW transect.

Apparently, the TDIC (HCO_3+CO_3 in Figs. 10A and 10B) in the water samples was a mixture of the inorganic and biogenic carbonates. The inorganic source of TDIC could be from the calcite/dolomite dissolution. The biogenic source of TDIC could be from the oxidation of organic matters by sulfate and iron-oxy-hydroxide (FeOOH), following the reactions (9) and (10) [33-35].

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad (9)$$

$$CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O \qquad (10)$$

The reactions (9) and (10) would lead the pH of the groundwater to be buffered within a range of 6.5-7.5 as it was seen from Table 2. The organic matters (CH_2O) participating in the reactions (9) and (10) are products of the bio-mineralization of the plant remnants co-deposited with sediment, and the FeOOH was an unavoidable constituent of the aquifer sediment. The source of sulfate in the groundwater could partly be from the seawater entrapped in the pores of the aquifer sediment, and partly from the gypsum dissolution (reaction 11).

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \qquad (11)$$
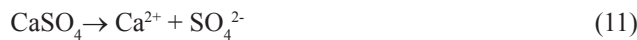
The calculation of the saturation index (SI) for gypsum in all the studied aquifers showed that the mineral dissolves, as its SI<0 (results of the calculation not shown here). Evidence for the sulfate reduction by organic matters in the aquifer sediment (reaction 9) is the trend of TDIC content increase with the increase of sulfate concentration in groundwater samples as shown in Fig. 11.
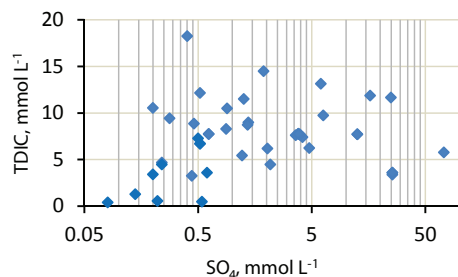

Fig. 11. A scatter plot of the TDIC content vs. [SO_4^{2-}] showing the possible oxidation of organic matter by sulfate in groundwater (reaction 9) in the MKRD. The concentration of SO_4^{2-} was expressed in the logarithmic scale.

The oxidation of organic matters (reactions 10 and 11) in water would make the carbon in TDIC get depleted by the heavy ^{13}C isotope [36].

The aquifers' sediment in the MKRD was of fluvial-marine nature that could contain not only plant remnants but also biogenic carbonate, such as shells, skeletal debris etc. containing high Mg-calcite. Therefore, the incongruent dissolution [36] of the Mg-calcite could be expected to occur within aquifers as it was usually observed in marine sediments (reaction 12).

$$Ca_{1-x}Mg_xCO_3 \rightarrow a.Ca_{1-y}Mg_yCO_3 + (x-ay).Mg^{2+} + (1-x-a+ay).Ca^{2+} + (1-a).CO_3^{2-} \qquad (12)$$
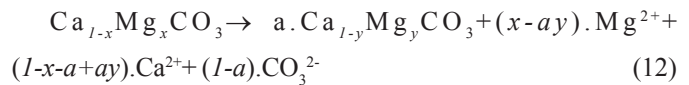
Reaction (12) would lead to the enrichment of $\delta^{13}C$ in the TDIC [6], because the carbon-13 signature in shells is more enriched compared with those in the organic matters. Gillikin, et al. [37] have found that the $\delta^{13}C$ in the shells of *Mytilus edulis* ranges from -3.0‰ to -7.7‰ *vs.* VPDB, independent of the temperature, that was much enriched compared with the $\delta^{13}C$ in C3 plant remnants (-23‰ *vs.* VPDB). The incongruent dissolution of Mg-calcite would also increase the Mg^{2+} concentration in water [6]. In fact, in this study, the concentration of a Mg^{2+} ion in most of the groundwater samples from the Mekong river delta was found to be higher than those of Ca^{2+} (Table 2).

Apparently, the contribution of carbonate from the reactions (9 and 10) and the reaction (12) to TDIC in groundwater in the MKRD was different in each sampling well, so the composition of carbon-13 ($\delta^{13}C$) in the TDIC ranged from -3.2‰ to -18.0‰ *vs.* VPDB as shown in Table 1 and Fig. 12.
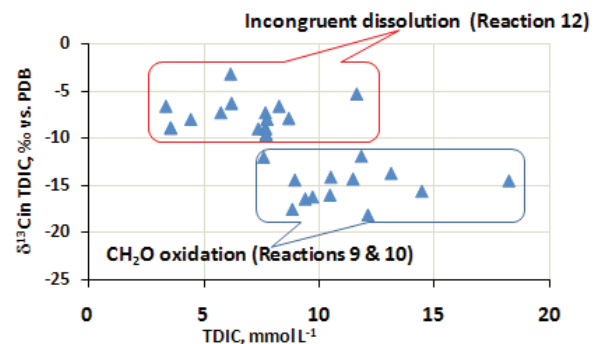

Fig. 12. A scatter plot of carbon-13 composition *vs.* TDIC content in groundwater throughout the MKRD: there are at least three geochemical reactions [(9), (10), and (12)] controlling the chemistry of groundwater in the MKRD.

As seen from Fig. 12, the trend of the $\delta^{13}C$ variation with the TDIC concentration in groundwater in the deep aquifers in the MKRD is that the more depleted the ^{13}C signature, the higher would be the concentration of TDIC in water. This indicates that the oxidation of organic matters by sulfate and iron oxyhydroxide, i.e. reaction (9) and (10) governs the TDIC content in the groundwater of the deep aquifers in the MKRD.

Conclusions

In the Mekong river delta, the groundwater in the Pleistocene, Pliocene, and Miocene aquifers was likely connate or very weakly recharged from the remote areas at a slow rate as it was evident from the ^{14}C-ages and water stable isotopic composition. This implies that the groundwater resource in that region is limited. The groundwater in the deep aquifers in the study region comprises the brackish, saline, and fresh types. The saline water in the deep aquifers could

result from the diffusion of saline pore water and salt intrusion into fresh water resources. The chemistry of groundwater is controlled by the oxidation of the organic matters and the incongruent dissolution of Mg-calcite. The heavy mining rate of groundwater today could cause inter-aquifer leakage and up conning of saline water, leading groundwater resources in the delta region to be deteriorated. This requires the development of appropriate measures for the better management of the groundwater resources in the entire MKRD region. Among others, artificial recharge with water from the Mekong river system could be considered to have a sustainable resource of freshwater for the region.

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