

Characteristics on distribution of chemical composition in groundwater along the Mekong and Bassac (Hậu) river, Vietnam

Hikaru Sato^{1*}, Naoaki Shibasaki², Nguyen Van Lap³, Ta Thi Kim Oanh³, Nguyen Thi Mong Lan³

¹*Graduate School of Symbiotic Systems Science and Technology, Fukushima University, 1 Kanayagawa, Fukushima City, Fukushima 960-1296, Japan*

²*Faculty of Symbiotic Systems Science, Fukushima University*

³*Ho Chi Minh City Institute of Resources Geography, Vietnam Academy of Science and Technology*

Received 18 January 2019; Received in revised form 10 July 2019; Accepted 15 July 2019

ABSTRACT

Along the Mekong River (MR), arsenic contamination in the groundwater has been recognized since the 2000s. Due to arsenic contamination in shallow aquifers, the drinking water has been prevented from being contaminated with arsenic by installing wells, 200 m to 400 m deep. However, it has been known that groundwater was contaminated by not only arsenic but also other trace elements. The need to reveal characteristics on the distribution of chemical composition by horizontally and vertically is increasing for purposes of appropriate development and management of groundwater. This study summarized the results of surveys for arsenic since 2008 and surveys for dissolved ions and trace elements since 2015, and described characteristics on distribution for chemical composition at the regional areas along the MR and Bassac (Hậu) River (BR). Groundwater samples were collected from existing wells in 8 provinces and 1 city. The authors used Piper and Stiff diagrams that reflect the chemical composition of groundwater to respond to varying horizontal and vertical distributions. The Principal Component Analysis (PCA) was also carried out to reveal the correspondences of dissolved ions and trace elements. A variety of concentrations and distributions of ions and trace elements show the obvious distinction between upper (<200 m deep) and lower (>200 m deep) aquifers broadly divided by geologic age. A wide variety of ion compositions and trace elements was found in the upper aquifer, and concentration of some trace elements in groundwater was high and exceed the World Health Organization (WHO) drinking water guideline value. On the other hand, groundwater in the lower aquifer is simple in chemical composition and rarely contaminated by trace elements. However, the arsenic concentration ranging from 0.01–0.065 mg/L slightly exceeding the WHO guideline value was found at the lower aquifer in the downstream areas of the MR Delta. These results on the distribution analysis provide the insight that deep groundwater is not necessarily safe by over-pumping from deep aquifers and drilling of new wells in the downstream areas.

Key words: Dissolved ions; trace elements; groundwater quality distribution; the Mekong River; the Bassac (Hậu) River.

©2019 Vietnam Academy of Science and Technology

1. Introduction

The Mekong River Delta (MRD) is located

in southern Vietnam. The delta is formed along the Mekong River (MR) and Bassac (Hậu) River (BR) (Fig. 1). The population in the study area was estimated at about

*Corresponding author, Email: s1771001@ipc.fukushima-u.ac.jp

18 million inhabitants (GSO, 2016). The rainy season lasts from May to November and some areas are affected by flooding (Fabrice and Claudia, 2012). The dry season lasts from December to April and the coastal areas are affected by seawater intrusion. Groundwater is one of the most important freshwater resources for residents in the MRD. In the 2000s, arsenic contamination was found in the MRD, then researchers had investigated and revealed the distribution and released mechanism of arsenic (e.g., Berg et al., 2007, Shinkai et al., 2007, Nguyen et al., 2008, Hoang et al., 2010, AAN and Mekong Group, 2012). These studies describe that high arsenic contamination in groundwater was most common in the shallow aquifer from the upstream areas and decreased to the downstream areas along the MRD. However, the groundwater arsenic contamination is not only in shallow wells, but also in deep wells (>200 m deep), and the arsenic contamination at the deeper depth has been reported by recent studies (Nguyen and Itoi, 2009, Erban et al., 2013, Merola et al., 2015). Erban et al. (2013) showed about 84% of wells of 170 to 150 m deep were contaminated by arsenic. Studies done by Buschmann et al. (2008) revealed that groundwater in southern Vietnam and bordering Cambodia is generally contaminated by the high concentration of not only arsenic but also some other trace elements. Shinkai et al. (2007) also showed the groundwater along the MR is contaminated by arsenic, manganese, and barium. Recent studies such as Tran et al. (2014a, 2014b) and Hoang and Bäumle (2019) revealed characteristics of ions and stable isotopes composition at Soc Trang Province located at the downstream area of the BR. However, characteristics of the horizontal and vertical distribution of groundwater quality such as dissolved ions and trace elements in the regional areas along the MR and BR are less documented. It is

needed to reveal the distribution of groundwater quality for purposes of appropriate development and management of groundwater. In particular, the development of deep groundwater from 200 m to 400 m is increasing for drinking and industrial purposes for major cities/provinces in the MRD.

The Research Group for Groundwater Contamination by Arsenic in the MRD (hereafter, the Mekong Group) has conducted groundwater surveys since 2008. The relationships between hydrogeological background and arsenic contamination in Tay and Gieng islands in Dong Thap and An Giang provinces had been identified from 2008 to 2012 (AAN and Mekong Group, 2012). Since 2013, the study area has been expanded to the downstream areas of the MR and BR deltas to clarify the situation of arsenic contamination in groundwater (Ito et al., 2016). Since 2015, dissolved ions and trace elements in groundwater have been analyzed to figure out contaminants and distribution of chemical composition, besides arsenic along the MR and BR deltas. This paper summarizes the results of the field surveys said above by the Mekong Group. The paper also elucidates that the horizontal and vertical distributions of groundwater quality along the MR and BR and the relationship between ion compositions and trace elements from 2015 to present (only arsenic data from 2008). This paper can assist groundwater development and management strategies for SDGs.

2. Methodology

2.1. Investigated wells and sample collection

The study area is located in the upstream and downstream areas along the MR and BR deltas (Fig. 1). Investigated wells were selected by officers of each province/city after we had designated the investigated area. The investigated wells are for domestic, industrial,

agricultural and drinking water supplies. A total of 315 wells ranging from 5 to 480 m deep were investigated. General information such as well depth, pumping rate, the purpose of use, etc. was obtained by hearing survey. Groundwater samples were collected after stagnant water in the well was removed. Actually, it was difficult to determine the sampling depth of each well, because the

screen depth(s) and number of screen location(s) vary by well. Therefore, the depth of groundwater collection was regarded as the well's depth in this study. Field values of pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were measured by using a portable pH/EC meter and an ORP meter (TOA DKK) at every 2, 5, and 10 minutes after groundwater sampling.

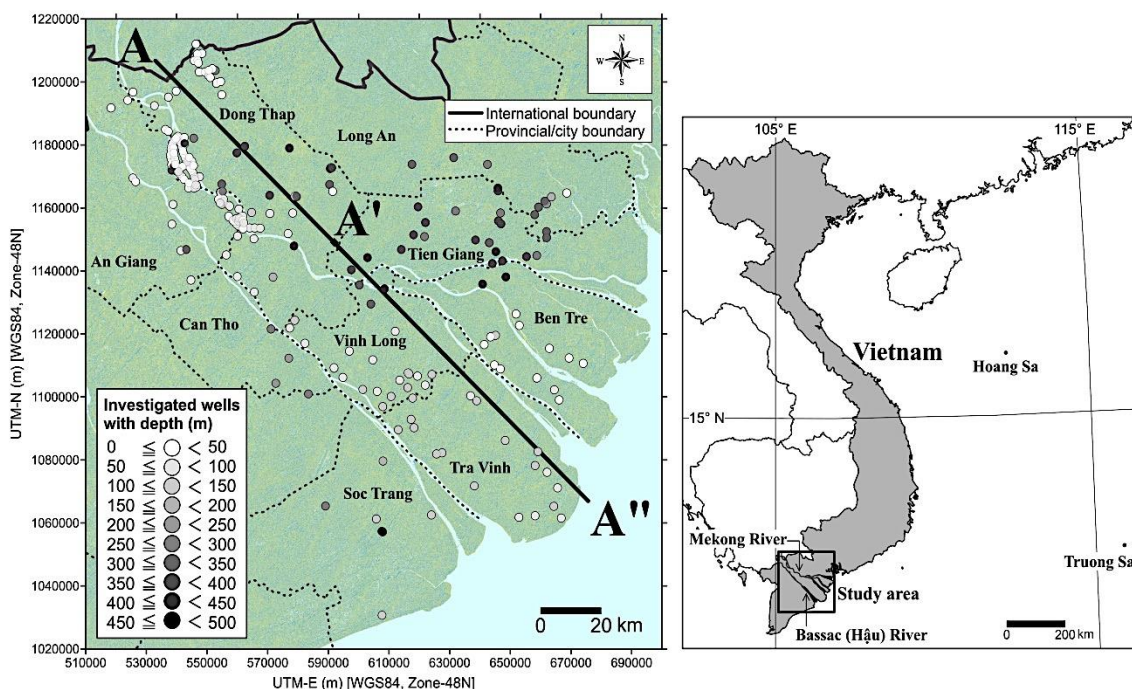


Figure 1. Location map of investigated wells with well depth. Study area is along the MR and BR, southern Vietnam. A, A' and A'' are used as cross section lines at Figs. 4–10 and Fig. 13

Field measurement of arsenic was analyzed by using the colorimetric method of the field test kit developed by Hironaka (1998). Groundwater samples for trace elements analysis were acidified with nitric acid then stored in two 100 mL sample bottles. Groundwater samples for analysis of dissolved ions were stored in 100 mL bottles so as to prevent air entering. These samples were kept under the low-temperature condition until the analysis was completed.

2.2. Chemical analysis

Groundwater samples collected from all investigated wells were sent to Japan for chemical analysis after the survey. Cations and anions of K^+ , Li^+ , Na^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_2^- , Br^- , SO_4^{2-} , NO_3^- and PO_4^{3-} were measured by ion chromatography using ICP-1000 and 2000 (DIONEX) at the laboratory in Fukushima University. The value of HCO_3^- was measured by pH 4.8 alkalinity titration method (JIS standard: JIS K 0101 13.1) using

sulfuric acid and bromocresol green methyl red. Trace elements were analyzed at the Niigata Prefectural Institute of Public Health and Environmental Sciences and the Fukushima Medical Device Development Support Centre, Japan. A total of 23 trace elements viz. Pb, Cr, Cd, Sb, Ti, As, Se, V, Co, Ni, Ga, Rb, Li, Al, Cu, Zn, Mn, Fe, Sr, Ba, Mo, Si and U were measured by the method of inductively coupled plasma mass spectrometer (ICP-MS) by using iCAP Qc (Thermo Fisher SCIENTIFIC) and 7800 ICP-MS (Agilent).

2.3. Classification of depth

The MRD is mainly composed of Neogene, Pleistocene and Holocene sediments, and it is described as a great flat plain (Nguyen et al., 2000, AAN and Mekong Group, 2012, Fabrice and Claidia, 2012). These strata mainly consist of sand and clay. Clay layers divide sand layers into some aquifer units.

AAN and Mekong Group (2012) described that the base of the Quaternary deposits was found at 122 to 218 m below ground level. Fabrice and Claidia (2012) also described that the top of Neogene deposit was detected at 80 up to 200 m below ground level. Therefore, the boundary of Quaternary and Neogene

deposits was assumed to be 200 m deep in this paper. The vertical distribution of chemical composition was organized with upper (<200 m in depth) and lower (>200 m in depth) aquifer by the boundary.

3. Results

3.1. Field measurements

The field measurements of groundwater collected from 2008 to 2017 are listed in Table 1. The investigated wells have a bias against well's depth by province/city because the predisposition of well's depth selection by officers was different by each province. Most wells with >100 m in depth are used for water supply. Groundwater temperature of all wells shows around 30°C. The pH values at all investigated wells are ranging from 3.6 to 8.8. The pH values of groundwater in Can Tho City and Tien Giang Province are slightly higher than other provinces (average values are 7.8 and 7.7, respectively). Average value of EC is the smallest in Tien Giang Province (75 mS/m). On the other hand, the average values are higher in Ben Tre and Vinh Long provinces (250–300 mS/m). In most investigated provinces, the average values of ORP show negative, whereas those in Can Tho City and Tien Giang Province show positive values.

Table 1. Summary of field measurements in 2008-2017. (Max: maximum, Min: minimum, Ave: average, Med: median, EC: electric conductivity, ORP: oxidation-reduction potential)

Province/City	No. of wells	Well depth (m)				Water temperature (°C)				pH				EC (mS/m)				ORP (mV)			
		Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med
An Giang	65	397	8	61	59	33.7	27.7	28.9	28.8	8.3	6.2	7.0	7.0	571.0	21.7	177.0	128.2	581	-154	-17	-38
Ben Tre	17	420	5	88	12	35.0	27.6	29.9	29.2	8.6	6.6	7.3	7.1	582.0	89.7	283.2	233.0	77	-144	-73	-85
Can Tho	4	295	202	252	256	35.4	31.6	33.9	34.4	8.1	7.0	7.8	8.1	147.3	55.6	117.6	133.7	229	-3	88	63
Dong Thap	145	480	9	73	32	35.5	27.1	29.4	29.0	8.8	3.6	6.9	7.0	1087.0	15.0	168.3	97.7	251	-203	-32	-57
Long An	12	340	32	276	319	34.3	29.3	32.7	33.1	7.4	6.1	6.8	6.8	712.0	30.1	114.1	41.4	114	-75	-10	-22
Soc Trang	8	480	125	279	205	39.4	30.8	34.0	31.6	8.0	6.1	7.3	7.3	241.0	74.6	163.7	178.6	-40	-84	-63	-67
Tien Giang	22	420	275	362	380	37.2	29.1	34.3	34.6	8.2	6.9	7.7	7.7	216.0	43.4	75.0	55.7	148	-103	45	66
Tra Vinh	17	125	85	107	110	30.7	28.4	29.5	29.3	7.4	6.9	7.1	7.2	259.0	65.2	115.1	91.1	-29	-117	-78	-84
Vinh Long	25	430	70	131	97	36.8	28.3	29.8	29.0	8.3	6.7	7.2	7.1	901.0	65.6	250.0	157.5	156	-119	-37	-72

3.2. Laboratory analysis

3.2.1. Characteristics of ion compositions and distributions

The analytical data of dissolved ions were shown in Table 2 and plotted on Piper

diagram (Fig. 2) and Stiff diagram (Figs. 3 and 4).

As shown in Fig. 2, most of Tien Giang samples (TG) are characterized by deeper groundwater (Na-HCO₃ type). Can Tho and Soc Trang samples (CT and ST) are plotted

near the boundary between Na-HCO₃ type and Na-Cl type. Most Ben Tre samples (BT) are characterized by Na-Cl type of saline water, whereas most Tra Vinh samples (TV) are characterized by shallow groundwater and fresh water. Groundwater samples of TV and Ving Long (VL) are plotted at the lower right domain of Ca(Mg)-HCO₃ type. Therefore, these groundwater samples contain slightly more Na+K than general freshwater type. The samples of VL have various types, most of the samples are plotted at upper domains of

mixed type and Na-Cl type. The cation composition shown in the lower left diagram, indicates that they are aligned on straight lines. This shows that the cation composition is controlled by the concentration of Na+K.

Stiff diagrams of horizontal and vertical distributions are shown in Figs. 3 and 4. Information of actual screen depths could not be obtained in this study, therefore samples were plotted at each depth of well bottom in the vertical distribution (Fig. 4).

Table 2. List of concentration of ions that mainly determine the groundwater composition

Province/ City	Na ⁺ +K ⁺ (mg/L)				Mg ²⁺ (mg/L)				Ca ²⁺ (mg/L)			
	Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med
Ben Tre	9.7E+02	1.2E+02	4.2E+02	3.2E+02	3.5E+02	6.3E+00	7.8E+01	5.5E+01	7.5E+02	3.0E+01	1.1E+02	6.5E+01
Can Tho	2.9E+02	7.6E+01	2.3E+02	2.8E+02	1.8E+01	3.1E+00	1.0E+01	9.3E+00	1.7E+01	9.0E+00	1.3E+01	1.3E+01
Soc Trang	5.5E+02	5.8E+01	2.6E+02	2.4E+02	5.1E+01	0.0E+00	2.6E+01	3.2E+01	5.6E+01	0.0E+00	2.8E+01	3.3E+01
Tien Giang	1.6E+02	5.1E+01	1.1E+02	1.1E+02	7.0E+01	3.2E+00	1.6E+01	9.9E+00	1.5E+02	7.6E+00	3.7E+01	2.5E+01
Tra Vinh	2.6E+02	6.0E+01	1.0E+02	7.9E+01	1.3E+02	2.2E+01	5.2E+01	4.5E+01	1.1E+02	2.4E+01	5.0E+01	5.2E+01
Vinh Long	1.5E+03	7.5E+01	3.5E+02	1.7E+02	1.3E+02	2.0E+00	6.0E+01	5.9E+01	1.6E+02	5.3E+00	7.9E+01	7.4E+01

Province/ City	Cl ⁻ (mg/L)				SO ₄ ²⁻ (mg/L)				HCO ₃ ⁻ (mg/L)			
	Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med
Ben Tre	3.0E+03	1.2E+02	7.2E+02	4.5E+02	2.7E+02	0.0E+00	8.7E+01	4.9E+01	8.6E+02	2.3E+02	4.4E+02	3.8E+02
Can Tho	2.2E+02	7.0E+00	1.3E+02	1.5E+02	1.1E+02	3.5E+01	7.0E+01	6.7E+01	4.4E+02	2.8E+02	3.8E+02	4.0E+02
Soc Trang	4.7E+02	8.7E+00	2.1E+02	1.9E+02	3.0E+02	1.1E+01	1.2E+02	1.2E+02	5.7E+02	6.4E+01	3.5E+02	3.4E+02
Tien Giang	5.3E+02	1.2E+00	9.7E+01	2.6E+01	6.2E+01	3.5E+00	1.6E+01	8.3E+00	3.4E+02	2.2E+02	2.8E+02	2.9E+02
Tra Vinh	4.9E+02	0.0E+00	7.6E+01	3.0E+01	4.5E+02	1.4E+01	9.7E+01	7.3E+01	5.0E+02	3.1E+02	4.1E+02	4.1E+02
Vinh Long	2.9E+03	9.8E+00	5.6E+02	1.7E+02	5.0E+02	1.3E+00	1.4E+02	9.3E+01	5.3E+02	2.9E+02	3.5E+02	3.4E+02

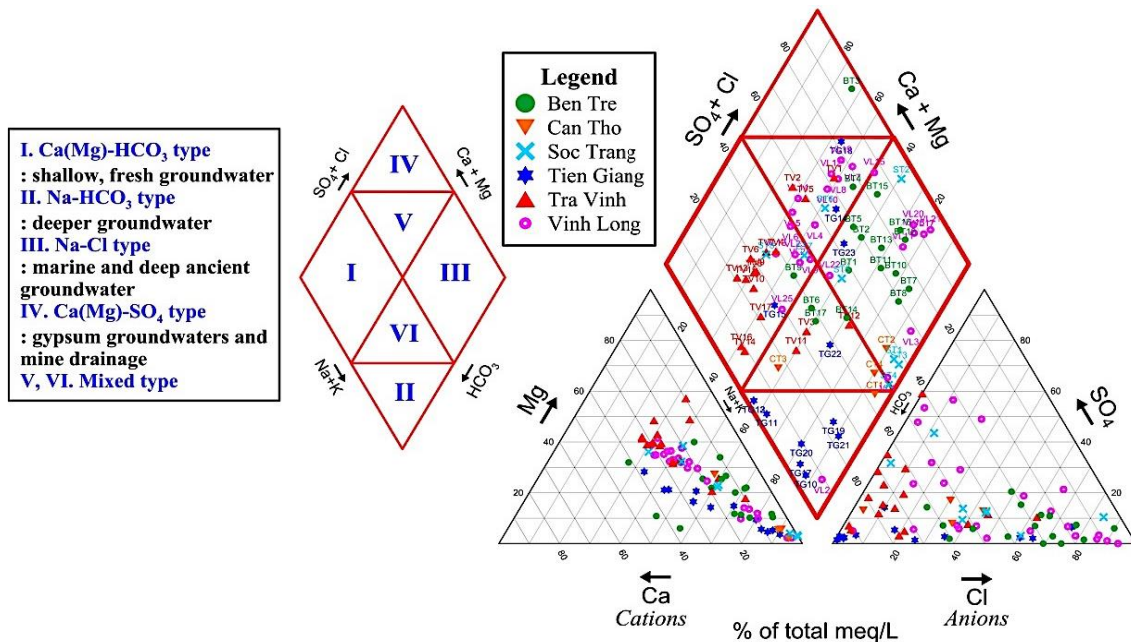


Figure 2. Piper diagram of groundwater samples

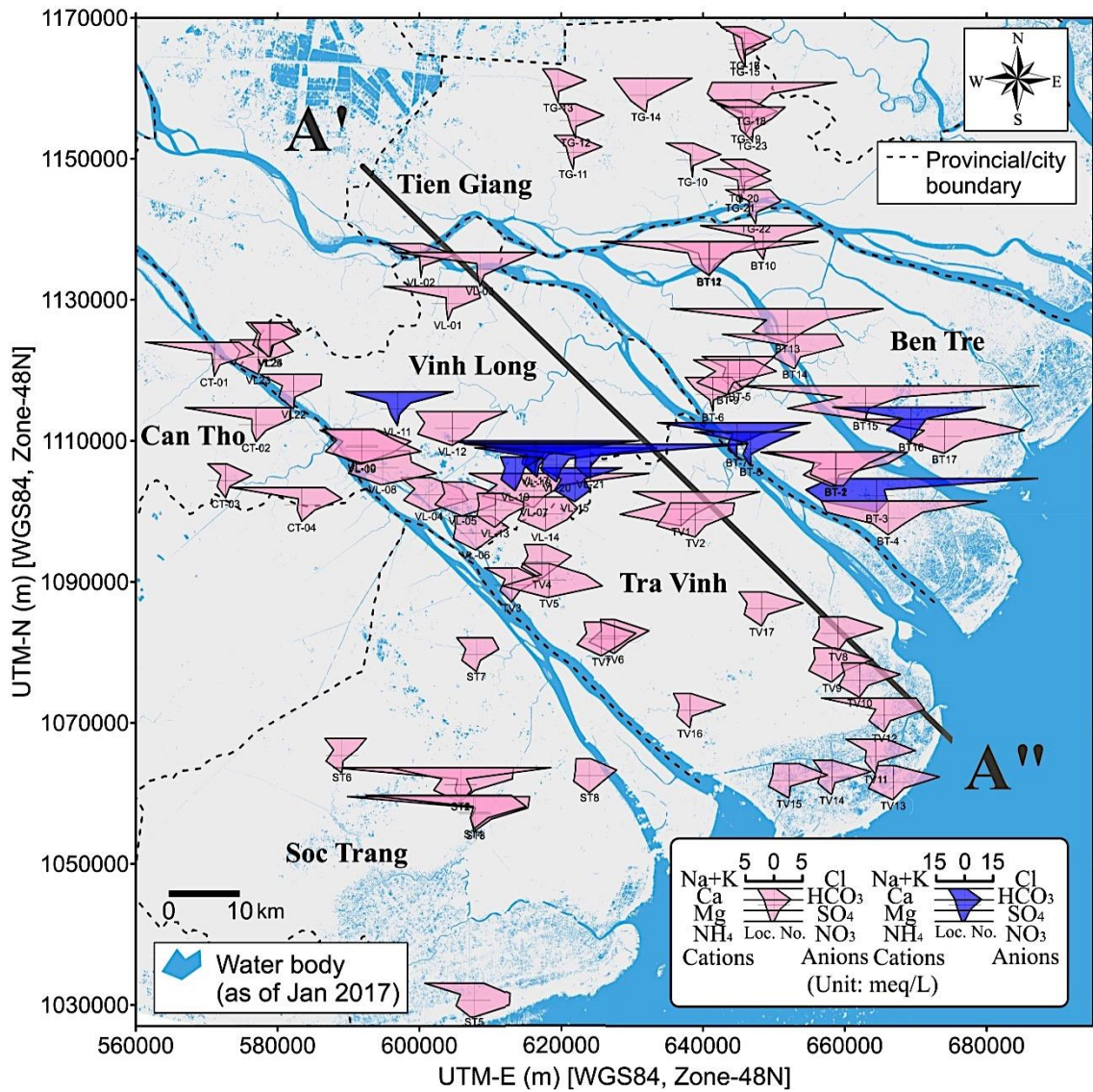


Figure 3. Horizontal distribution of Stiff diagrams and A'-A'' cross section line. Water body map is based on Landsat 8 (as of Jan 2017). Patterns having large amount of dissolved ions are shown by dark blue color

Ion compositions in the downstream areas along the MR and BR are divided into 4 types (viz. Na-HCO₃, Na-Cl, (Na+Mg)-HCO₃ and (Na+Mg)-SO₄ type) (Fig. 3). Most groundwater in Tien Giang Province shows Na-HCO₃ type with low concentration. High Na-Cl concentration type (EC is over 250 mS/m) were distributed in Ben Tre and central Vinh Long provinces. (Na+Mg)-HCO₃

type was distributed at Vinh Long and Tra Vinh provinces. It is noted that (Na+Mg)-SO₄ type was distributed along the left bank of the BR. Groundwater in Can Tho City and Soc Trang Province shows Na-Cl type, however, it also contains HCO₃⁻ and shows low concentration of the dissolved ions than Na-Cl type in Vinh Long and Ben Tre provinces.

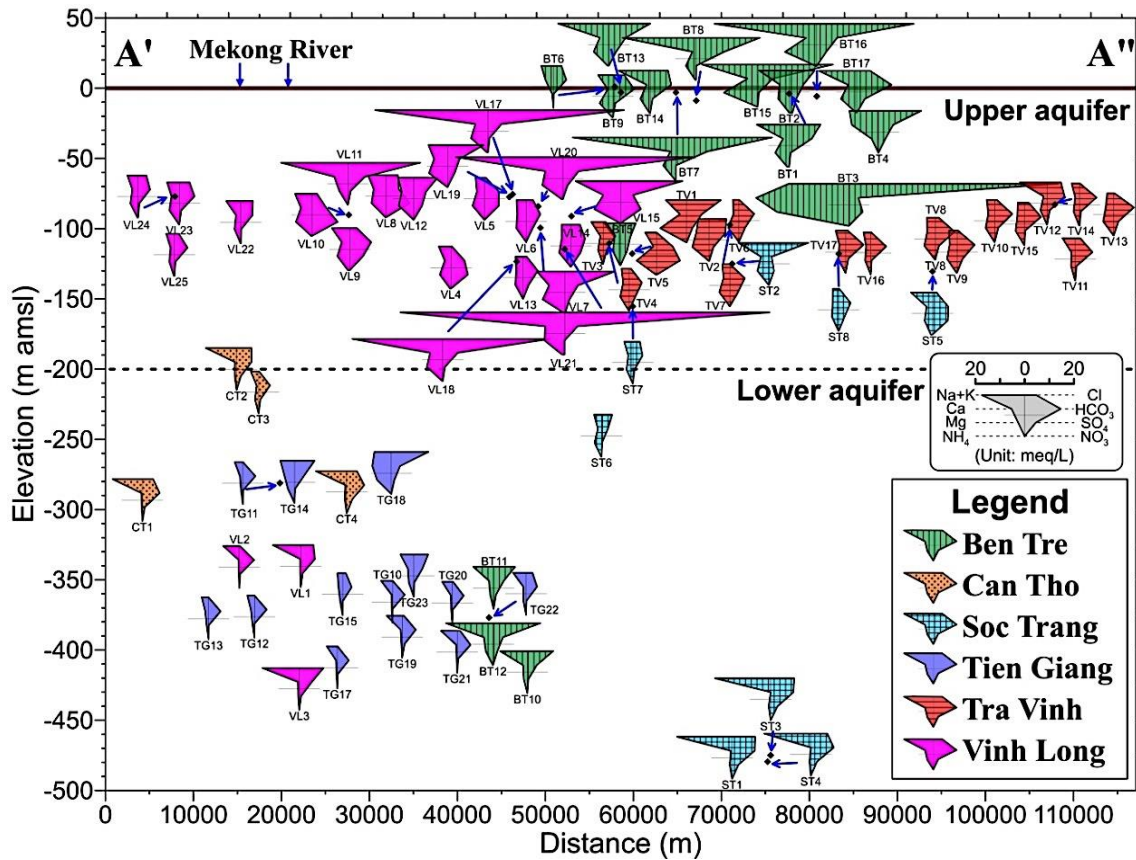


Figure 4. Vertical distribution of Stiff diagrams. Locations of all Stiff diagrams are projected in orthogonal direction to A'-A''

According to Fig. 4, Na-HCO₃ type and Na-Cl type with low concentration is distributed at the lower aquifer. On the other hand, groundwater in the upper aquifer shows high concentration of Na-Cl, (Na+Mg)-HCO₃ and (Na+Mg)-SO₄. In Ben Tre Province, Na-Cl type was found at wells shallower than 20 m deep. This type in central Vinh Long Province was also found locally at the depth from 80 to 130 m. (Na+Mg)-HCO₃ and (Na+Mg)-SO₄ types were found at depths from 80 to 170 m and from 80 to 130 m, respectively.

3.2.2. Characteristics of trace elements concentrations and distributions

Arsenic

The rate of samples exceeding the WHO

guideline value arsenic (0.01 mg/L; WHO, 2011) was 48% among the investigated wells. However, most of these samples were collected at Tay and Gieng islands in Dong Thap and An Giang provinces (Table 3 and Fig. 5a). High arsenic concentrations in the upstream areas are distributed like hotspots. The arsenic concentrations exceeding the WHO guideline value in the downstream areas were rarely seen in locations away from the MR and BR. However, a sample which concentration exceeding 0.2 mg/L was found in Ben Tre Province. The concentrations of 0.01–0.1 mg/L were distributed on the left bank side of the MR.

Vertical distribution of arsenic concentration was shown in Fig. 5b. The high

concentrations of arsenic were detected at the upper aquifer in the upstream areas. While concentrations slightly exceeding the WHO guideline value were found at the lower aquifer in Dong Thap, Long An, and Tien Giang provinces. However, the concentrations (0.01–0.065 mg/L) were clearly lower than shallow (<50 m in depth) wells of the upper aquifer.

Table 3. List of concentration of arsenic (mg/L)

Province/ City	As (mg/L)			
	Max	Min	Ave	Med
An Giang	1.2E+00	5.0E-04	4.9E-01	1.7E-01
Ben Tre	2.1E-01	4.0E-04	2.1E-02	3.0E-03
Can Tho	4.0E-03	1.0E-03	2.0E-03	2.0E-03
Dong Thap	1.8E+00	5.0E-04	7.1E-01	3.1E-01
Long An	6.5E-02	5.0E-03	1.6E-02	1.0E-02
Soc Trang	1.5E-02	1.0E-03	3.0E-03	2.0E-03
Tien Giang	2.5E-02	1.0E-03	1.1E-02	1.1E-02
Tra Vinh	6.0E-03	1.0E-03	2.0E-03	1.0E-03
Vinh Long	3.3E-02	3.0E-04	5.0E-03	1.0E-03

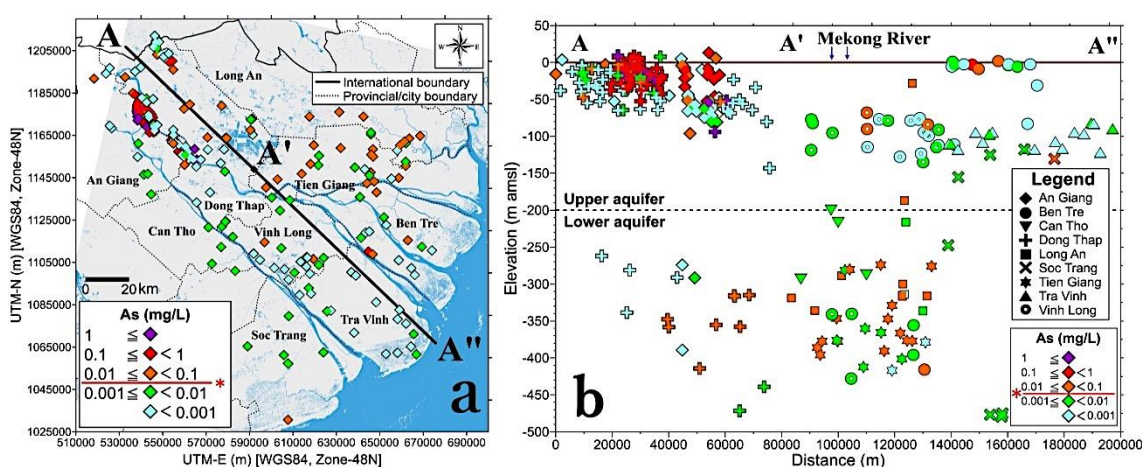


Figure 5. Horizontal and vertical distributions of arsenic concentration (a: horizontal distribution, b: vertical distribution), *is the upper limit of the WHO guideline value (0.01 mg/L)

Other trace elements

Various trace elements have been measured since 2015. The trace elements exceeding the WHO guideline value, except for arsenic, were found for manganese (0.4 mg/L) and barium (0.7 mg/L). Five trace elements, those concentrations exceeding the WHO/Vietnamese guideline values and showing characteristic distribution, are described in this section (Table 4).

(1) Manganese

The number of samples exceeding the WHO guideline value is 19. The maximum of 4.0 mg/L in manganese was found in Ben Tre Province. The samples having higher concentration of manganese were detected in central Vinh Long and Ben Tre provinces (Fig.

6a). Manganese concentrations exceeding the guideline value were found at a depth of <130 m in the upper aquifer (Fig. 6b).

(2) Barium

Barium concentrations exceeding the WHO guideline value were found at 2 wells (Fig. 7a). The depths of these samples are 285 and 120 m, respectively (Fig. 7b).

(3) Iron

Iron was often found in the groundwater along the MR. Although WHO (2011) does not show a health guideline value for iron, 0.3 mg/L was set by the Vietnamese guideline value (Ministry of Health, 2009). Samples exceeding the Vietnamese guideline value account for 64% of all samples. The maximum of 41 mg/L, which is significantly exceeding the guideline value was detected at

the upper aquifer in Soc Trang Province (Fig. 8a). Samples with higher concentration exceeding the guideline value are mainly distributed in the upper aquifer (Fig. 8b).

(4) Boron

Samples exceeding the WHO guideline value of boron (2.4 mg/L) were not found in the investigated wells. The maximum of 0.93 mg/L was found in Ben Tre Province. Boron concentration exceeding 0.3 mg/L (Vietnamese guideline value) was found only in a part of Can Tho City, Ben Tre and Soc Trang provinces (Fig. 9a). It never appeared in Vinh Long, Tra Vinh, and Tien Giang provinces. In Ben Tre Province, boron was found at a shallow depth of <20 m (Fig. 9b). In Can Tho

City and Soc Trang Province, it was distributed at depth of >200 m.

(5) Strontium

The health guideline value of strontium is not shown by the WHO guideline and the Vietnamese guideline. The maximum of 3.5 mg/L was detected in Ben Tre Province (Fig. 10a). However, samples having higher concentrations exceeding 1.0 mg/L show the following characteristic distribution. The concentration was detected at the interior of Vinh Long, a part of Ben Tre and Tien Giang provinces (Fig. 10a). Strontium concentration at the upper aquifer is higher than the lower aquifer.

Table 4. List of concentration of trace elements, those exceeding the WHO guideline values and showing characteristic distributions

Province/City	Mn (mg/L)				Ba (mg/L)				Fe (mg/L)			
	Max	Min	Ave	Med	Max	Min	Ave	Med	Max	Min	Ave	Med
Ben Tre	4.0E+00	1.4E-02	9.3E-01	4.6E-01	5.9E-01	4.0E-03	1.2E-01	3.7E-02	1.1E+01	4.0E-02	3.9E+00	1.6E+00
Can Tho	9.5E-02	8.0E-03	4.0E-02	3.0E-02	2.2E-01	1.4E-01	1.8E-01	1.8E-01	4.8E-01	2.0E-02	2.2E-01	1.9E-01
Soc Trang	1.1E+00	1.5E-02	2.0E-01	8.0E-02	4.3E-01	3.4E-02	1.5E-01	1.1E-01	4.1E+01	7.0E-02	5.8E+00	5.7E-01
Tien Giang	1.5E-01	8.0E-03	4.0E-02	3.0E-02	7.2E-01	7.6E-02	2.5E-01	2.1E-01	2.3E+00	2.0E-02	4.3E-01	7.0E-02
Tra Vinh	2.8E-01	2.4E-02	1.0E-01	6.0E-02	2.5E-01	2.0E-02	1.1E-01	9.0E-02	1.8E+00	1.0E-02	6.1E-01	4.7E-01
Vinh Long	3.8E+00	1.3E-02	6.4E-01	1.5E-01	2.4E+00	3.1E-02	2.7E-01	1.6E-01	6.7E+00	1.0E-02	1.2E+00	9.0E-01
Province/City	B (mg/L)				Sr (mg/L)							
	Max	Min	Ave	Med	Max	Min	Ave	Med				
Ben Tre	9.3E-01	4.0E-02	3.2E-01	1.3E-01	3.5E+00	2.8E-01	8.7E-01	6.1E-01				
Can Tho	7.8E-01	1.7E-01	4.7E-01	4.7E-01	2.1E-01	1.5E-01	1.8E-01	1.9E-01				
Soc Trang	7.6E-01	8.0E-02	3.7E-01	2.7E-01	6.3E-01	8.0E-02	3.1E-01	3.3E-01				
Tien Giang	8.0E-02	1.0E-02	4.0E-02	3.0E-02	1.3E+00	1.0E-01	4.1E-01	3.1E-01				
Tra Vinh	2.5E-01	9.0E-02	1.5E-01	1.5E-01	1.5E+00	2.3E-01	6.4E-01	5.5E-01				
Vinh Long	1.9E-01	8.0E-02	1.2E-01	1.2E-01	2.3E+00	8.0E-02	7.7E-01	6.2E-01				

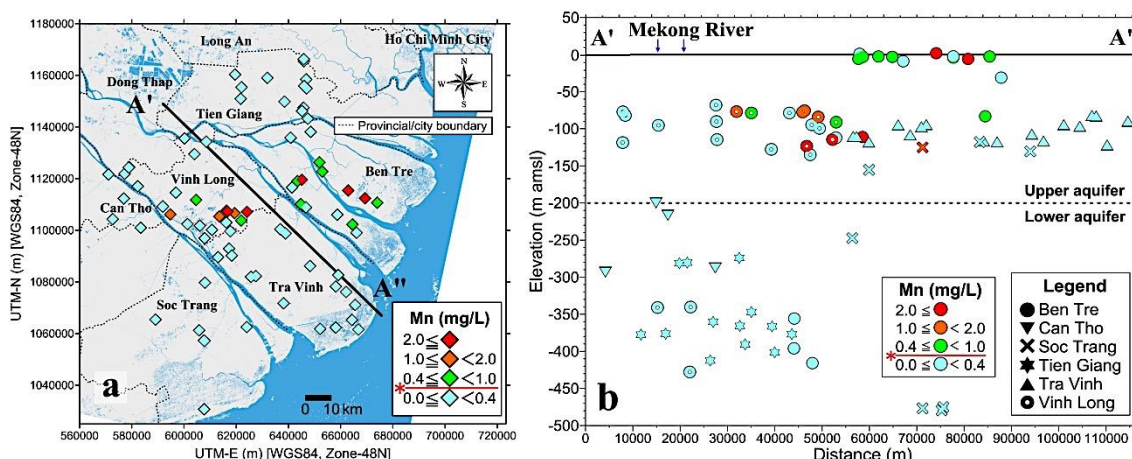


Figure 6. Horizontal and vertical distributions of manganese concentration (a: horizontal distribution, b: vertical distribution). *is the upper limit of the WHO guideline value (0.4 mg/L)

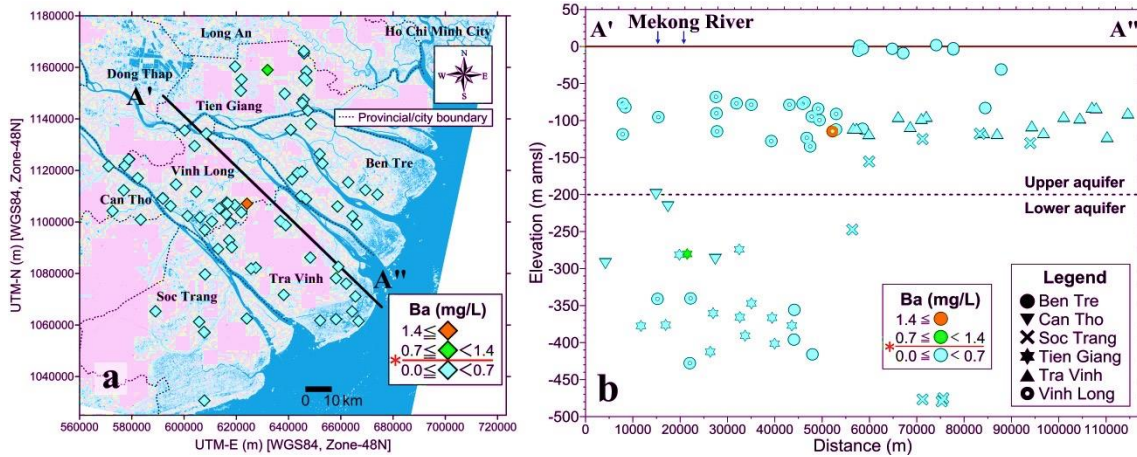


Figure 7. Horizontal and vertical distributions of barium concentration (a: horizontal distribution, b: vertical distribution). *is the upper limit of the WHO guideline value (0.7 mg/L)

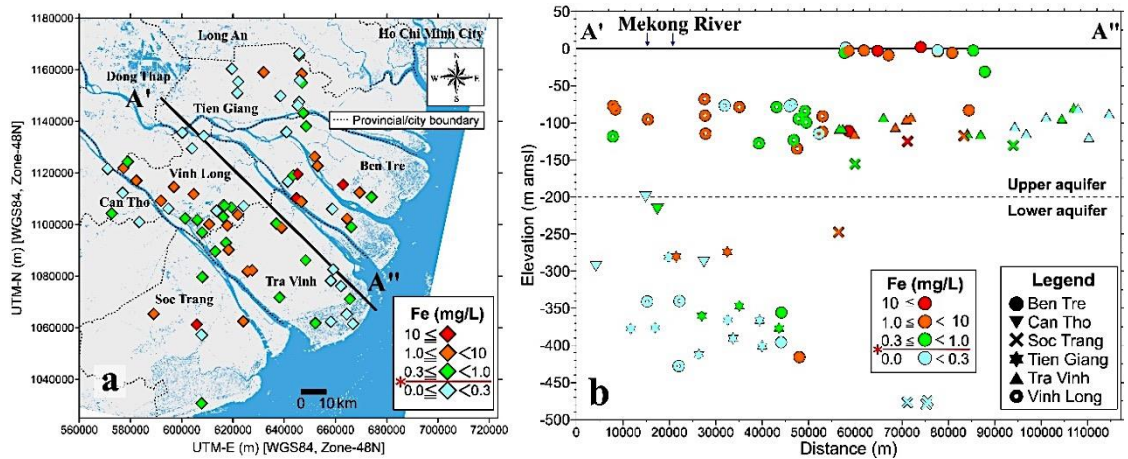


Figure 8. Horizontal and vertical distributions of iron concentration (a: horizontal distribution, b: vertical distribution). *is the upper limit of the Vietnamese guideline value (0.3 mg/L)

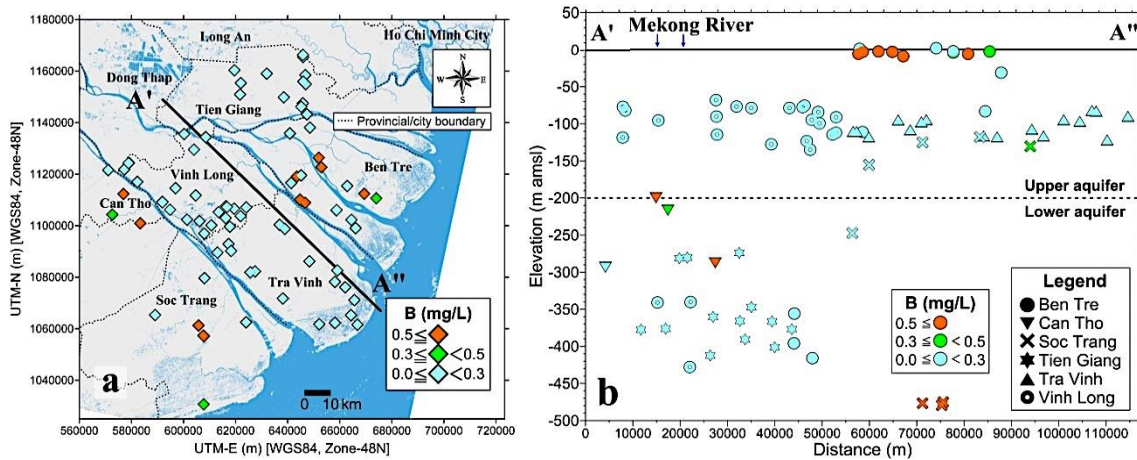


Figure 9. Horizontal and vertical distributions of boron concentration (a: horizontal distribution, b: vertical distribution). The WHO guideline value is 2.4 mg/L

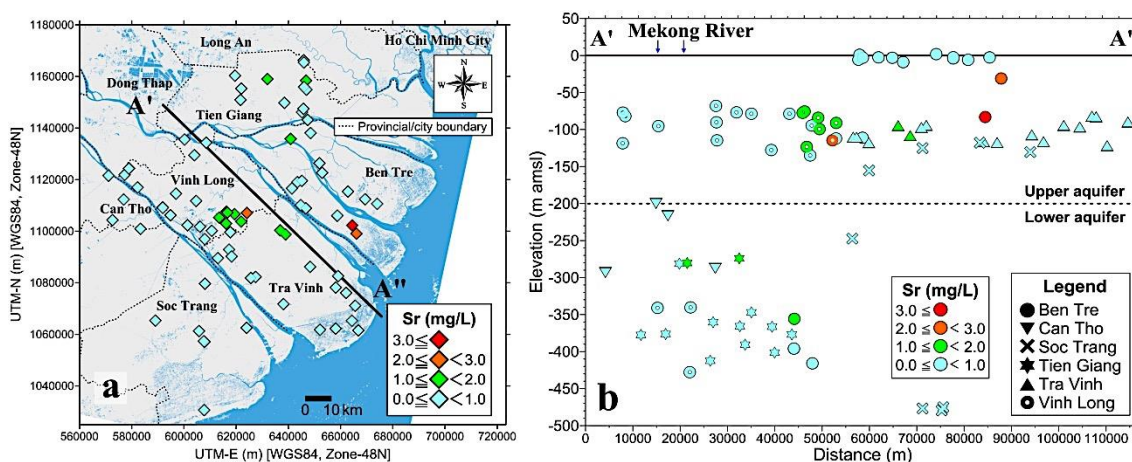


Figure 10. Horizontal and vertical distributions of strontium concentration (a: horizontal distribution, b: vertical distribution)

4. Discussions

4.1. Relationships between ion compositions and trace elements

Groundwater in the upper aquifer tends to contain various ions and trace elements with higher concentration from the results shown in Figs. 4–10. For consideration of relationships between ion compositions and trace elements, the Principal Component Analysis (PCA) was carried out. The concentrations below the detection limit (DL) of each element were replaced by DL/2 for the analysis. Furthermore, some trace elements which have no scattering were removed from the analysis. The PCA results of 25 chemical parameters in 83 groundwater samples are shown in Table 5 and Fig. 11.

Principle components affecting groundwater quality in the MRD were identified as shown in Table 5. Factor loading of F1 which explains 33% of total variables has high values on EC, Na⁺, and Cl⁻. F1 is likely to be a strong correlation with saline water having much-dissolved ions. The contribution of EC, Na⁺, and Cl⁻ to this factor is derived from the saline groundwater (Na-Cl type) at the MRD. F1 also has a strong correlation with Zn, Se, Sr, Cu, Mn, and Li,

which explains that groundwater originated from seawater contains a wide variety of trace elements. The results suggest that the groundwater of Na-Cl type in the MRD has high concentrations of trace elements due to long residence time. The factor loading of F2 which explains 13% of total variables has strong negative values on Ca²⁺ and Mg²⁺, whereas F2 has high positive values on HCO₃⁻ and B. This indicates that the concentrations of HCO₃⁻ and B increase, the concentrations of Ca²⁺ and Mg²⁺ decrease. In general, shallow groundwater shows Ca(Mg)-HCO₃ type (Fig. 2). As residence time of groundwater becomes longer and/or the occurrence depth becomes deeper, the concentration of HCO₃⁻ increases and ion exchange occurs from Ca²⁺ to Na⁺ (Appelo and Postma, 2005). Therefore, F2 is likely to show the difference in chemical composition between the shallow aquifer and deep aquifer. However, the factor loadings of Na⁺ and HCO₃⁻ in F2 are small, 0.38 and 0.65, respectively (Table 5). This reason is likely due to (Na+Mg)-HCO₃ type which has low concentrations of HCO₃⁻ at Vinh Long and Tra Vinh provinces (Fig. 11). The plot of PCA scores by F1 and F2 helps to understand the characteristics of chemical composition in the

MRD. High Na-Cl concentration type was plotted in the positive domain of F1. This domain was characterized by Ben Tre and Vinh Long provinces. In the negative domain of F1, samples of Can Tho City and Tien Giang, Soc Trang, Tra Vinh, and Vinh Long provinces were plotted. F2 reflects the ion exchange of groundwater. Accordingly, the negative domain is dominant for groundwater in Tra Vinh and Vinh Long provinces collected at relatively shallow depth (80–170 m) and the positive domain is dominant for groundwater in Can Tho City, Tien Giang, and Soc Tran provinces.

Table 5. Factor loadings of principal components on variables. Boldfaces are variables indicating that the factor loading are >0.8

Variables	F1	F2	F3
EC (mS/m)	0.928	0.175	-0.062
Cl ⁻ (mg/L)	0.919	-0.021	-0.199
Na ⁺ (mg/L)	0.830	0.380	-0.159
Zn (mg/L)	0.810	0.280	-0.068
Se (mg/L)	0.798	0.257	-0.338
Sr (mg/L)	0.772	-0.463	-0.072
Cu (mg/L)	0.730	0.327	-0.350
Mg ²⁺ (mg/L)	0.707	-0.483	0.312
Mn (mg/L)	0.696	-0.026	0.037
Li (mg/L)	0.610	-0.483	0.030
NH ₄ ⁺ (mg/L)	0.599	0.167	0.220
Ca ²⁺ (mg/L)	0.592	-0.553	0.015
Al (mg/L)	0.493	0.177	-0.059
Ba (mg/L)	0.425	0.088	-0.506
Ni (mg/L)	0.396	0.092	-0.091
K ⁺ (mg/L)	0.355	0.196	0.478
Fe (mg/L)	0.292	-0.089	0.110
As (mg/L)	0.243	0.455	-0.002
HCO ₃ ⁻ (mg/L)	0.170	0.647	0.581
B (mg/L)	0.148	0.692	0.453
SO ₄ ²⁻ (mg/L)	0.133	-0.327	0.508
Mo (mg/L)	0.061	0.509	0.422
ORP (mV)	-0.157	0.164	-0.714
Water temp (°C)	-0.445	0.310	-0.355
pH	-0.513	0.470	-0.296

According to Table 5 and Fig. 11, ion composition in the MRD was divided into high Na-Cl concentration type and other types ((Na+Mg)-HCO₃ and Na-HCO₃ types). This result was explained by the cation

composition in the Piper diagram (Fig. 2) which is controlled by the concentration of Na+K. It is presumed that Na-Cl type gives a great influence on the groundwater composition in the MRD.

4.2. Vertical distribution of arsenic and aquifers

The upper aquifer in the upstream areas is contaminated by high arsenic concentration exceeding 1.0 mg/L, and even the lower aquifer in the downstream areas is contaminated by arsenic (0.01–0.065 mg/L) slightly exceeding the WHO guideline value (Fig. 5). However, the depths where arsenic exceeds the WHO guideline value is limited, less than 70 m in the upper aquifer and 250–450 m in the lower aquifer (Fig. 12a). Despite the well's depths investigated in each province/city have a bias, the arsenic was detected at the similar depths of the upstream and downstream areas. Ion compositions of 100–250 m show (Na+Mg)-HCO₃ and (Na+Mg)-SO₄ types, that means the sediments at the depths are assumed to be non-marine sediments or relatively coarse-grained marine sediments. Arsenic is usually contained in fine-grained layers, and high arsenic concentration in groundwater is related to reductive dissolution (Wilkie et al., 1996; Nickson, 2000; AAN and Mekong Group, 2012). Although the groundwater at the depth from 100 to 150 m shows negative ORP values (93% of groundwater at the depth is under reducing condition), the groundwater at the depth is not contaminated by arsenic. Therefore, the sediments at the depth are likely not containing arsenic.

Relationships among well's depth, ORP value, and arsenic concentration indicate that groundwater in the upper aquifer has high arsenic concentration (>0.1 mg/L) with negative ORP value (Fig. 12b). On the other hand, groundwater in the lower aquifer is contaminated by arsenic slightly exceeding the WHO guideline value with both negative and positive ORP values.

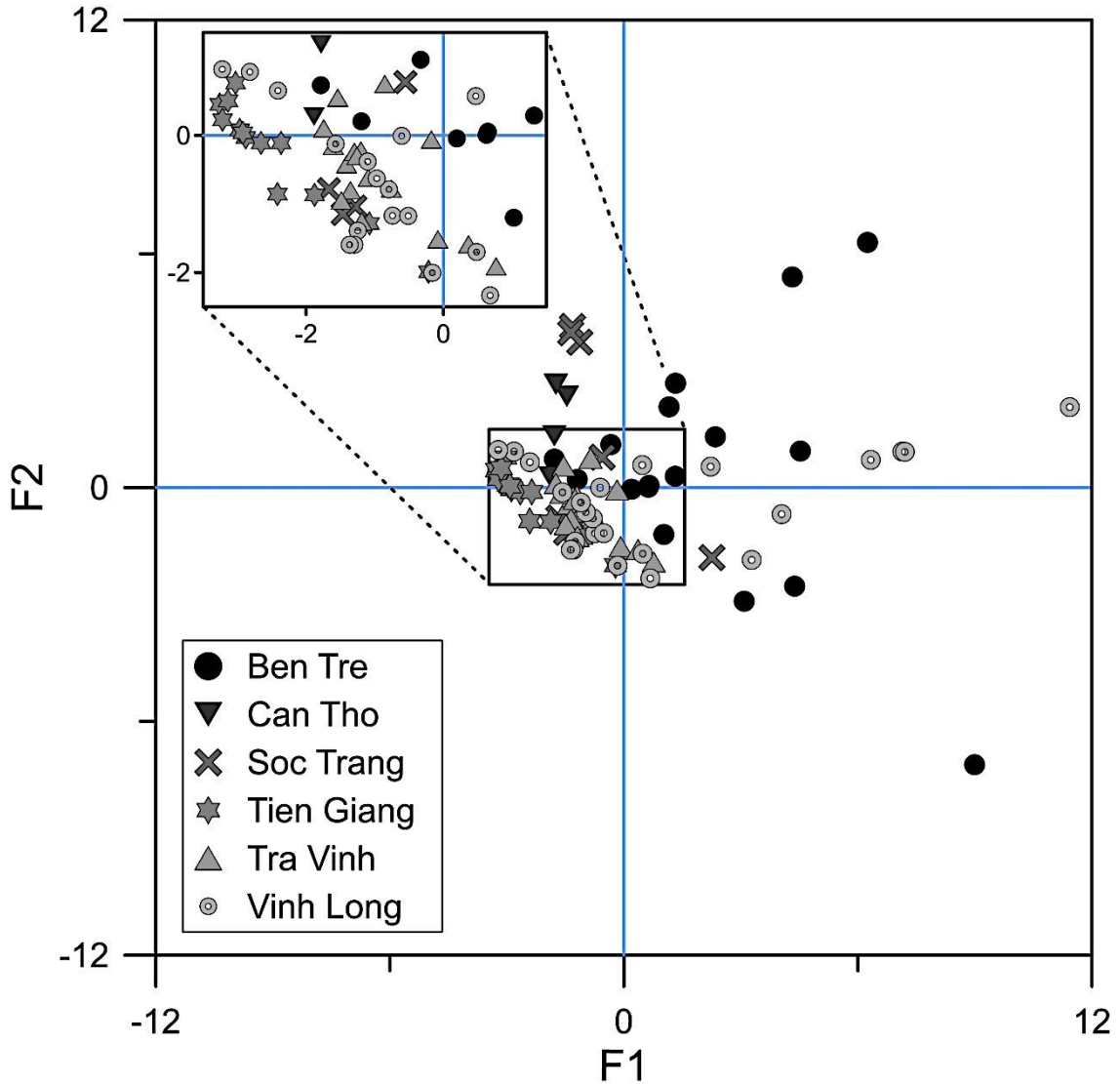


Figure 11. Plots of PCA scores between F1 and F2. Symbols are changed by each province/city

As the reasons that arsenic was detected with positive ORP value below 250 m in depth, three causes are discussed. The first cause is that arsenic occurs by oxidative decomposition of sulfide-bearing minerals such as pyrite (Nguyen and Itoi, 2009). However, it is a low possibility because iron and SO_4^{2-} in groundwater at depth (>250 m) show very low correlations against arsenic ($R= 0.04$ and 0.01). The second cause is due

to leakage and squeeze of clayey layers containing arsenic by excessive pumpage (Erban et al., 2013, Minderhoud et al., 2017). Nguyen and Itoi (2009) described that sediments containing arsenic are distributed at >200 m in depth at the upstream areas of the MRD. It is assumed that arsenic was forced to migrate from sediments containing arsenic to the sediments with positive ORP value due to leakage and squeeze, as described by Erban et

al. (2013). The third cause is a problem by unknown screen depth. Groundwater quality data were organized by well depth because information of screen depth was not obtained in this study. Results of ion compositions show some groups by each province/city and do not show clear possibility of mixing so that the effect is likely to be low. Relationships among well depth, ORP value, and arsenic

concentration suggest that it is necessary to observe arsenic concentration continuously, because rise of the arsenic concentration and the expansion of the distribution in the lower aquifer is likely to occur in future by the overexploitation and uncontrolled drilling of the aquifer for new deep wells in the downstream areas.

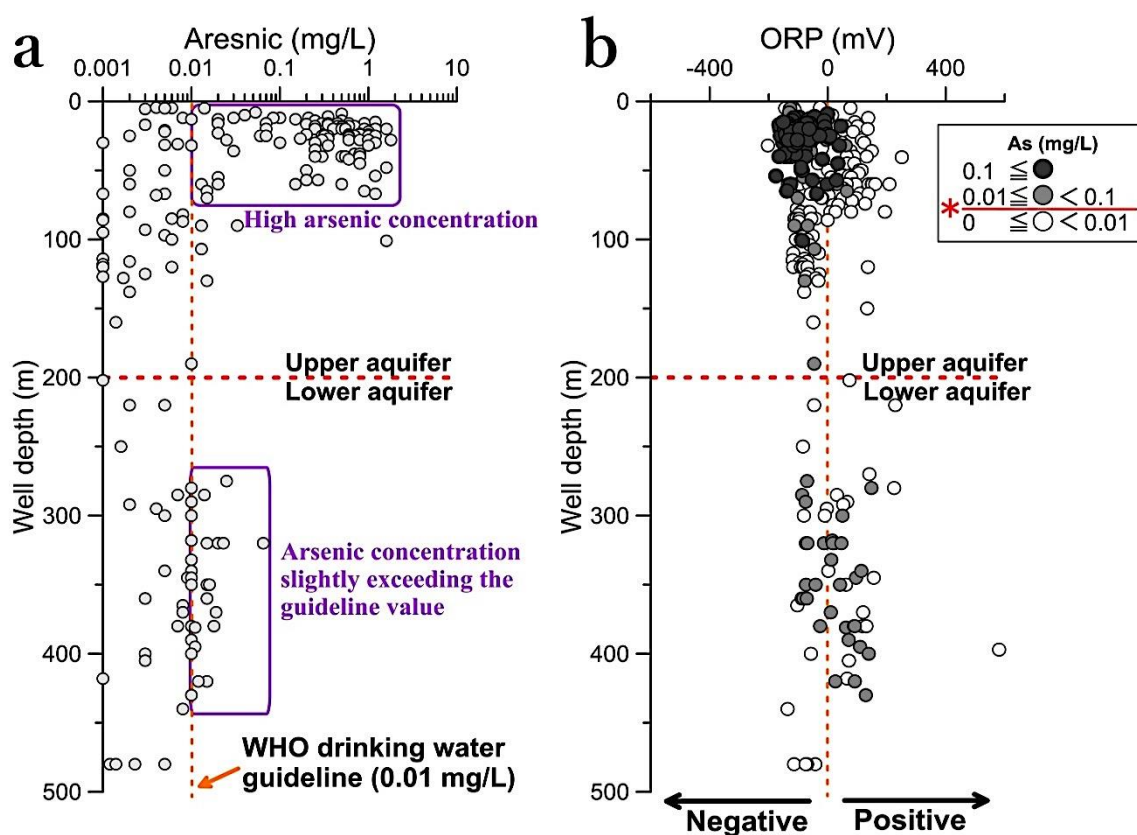


Figure 12. Distributions of arsenic concentrations and ORP values of the upper and lower aquifer. (a: arsenic concentration with depth, b: arsenic concentration and ORP with depth). *is the upper limit of the WHO guideline value (0.01 mg/L)

4.3. Characteristics on distribution of chemical composition along the MR and BR

Distribution of chemical composition was analyzed by horizontally and vertically, and it was revealed that different chemical composition occurs by region and depth (Fig. 13). As mentioned above, the ion composition

of the MRD was broadly divided into high Na-Cl concentration type and other types ((Na+Mg)-HCO₃ and Na-HCO₃ types). The distribution of groundwater which shows Na-Cl type in Vinh Long Province is limited and unique, because the depth in which the type was detected is deep (80–170 m) even though

other groundwater at the same depth shows fresh water such as (Na+Mg)-HCO₃ type and (Na+Mg)-SO₄ type. It is assumed that the aquifer of Vinh Long Province where the Na-Cl type is distributed had been affected locally by paleo-seawater. Hoang et al. (2019) also described that groundwater quality collected at the qp₂₋₃ aquifer (80–130 m deep) in Soc Trang Province is differ significantly in lateral

direction and groundwater at the aquifer is derived from seawater and freshwater sources. This results of the distribution and chemical composition of the upper aquifer at 80–130 m deep are similar to our study, and our study indicates that the groundwater composition at the depth in Vinh Long Province is also complex.

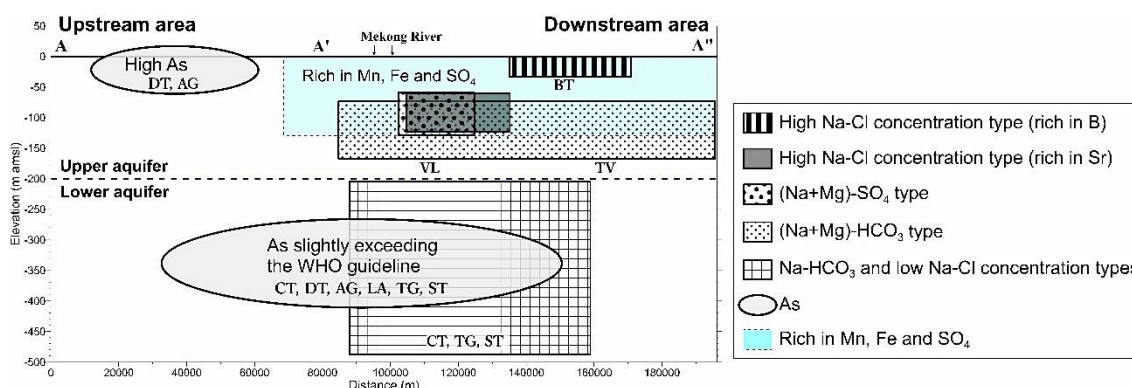


Figure 13. Characteristics of groundwater quality along the MR. Note that Dong Thap (DT) and An Giang (AG) provinces show high arsenic concentration (0.01–1.8 mg/L) at the depth of 0–70 m; low arsenic concentration (0.01–0.65 mg/L) is common at the depth of 250–400 m in Dong Thap (DT), An Giang (AG), Can Tho (CT), Long An (LA), Tien Giang (TG) and Soc Trang (ST) city/provinces. High Na-Cl concentration type is distributed at a shallow depth of 20 m in Ben Tre (BT) Province and at a depth of 80–130 m in Vinh Long (VL) Province. Na-Cl type rich in boron is found in Ben Tre Province and the type rich in strontium is found in Vinh Long Province. Tra Vinh (TV) and Vinh Long (VL) provinces are characterized by (Na+Mg)-HCO₃ type in 80–170 m deep. In Vinh Long (VL) Province, (Na+Mg)-SO₄ type is also distributed locally at 80–130 m deep. Low Na-Cl concentration type and Na-HCO₃ type are generally distributed in Can Tho (CT), Tien Giang (TG) and Soc Trang (ST) at a depth of over 200 m

Various ion compositions and trace elements were found in the upper aquifer more than lower aquifer. This suggests that the actual aquifers are more complicated, and the groundwater quality patterns would be subdivided by some reasons such as difference of recharge area, groundwater flow system, and multiple aquifer units. Sediments at depth <200 m are composed of younger formations in Quaternary. The complex paleo-topography and aquifer distribution formed by transgression and regression may have produced such diversity of water quality. On

the other hand, the groundwater quality in the lower aquifer is classified into Na-HCO₃ type and Na-Cl type with low concentration. The chemical composition in the lower aquifer is simpler than the composition in the upper aquifer.

Although the well's depths investigated in each area of province/city were biased and the screen depths were unknown, brief difference of chemical compositions in the MRD could be revealed by just classifying the groundwater samples into the upper and lower aquifers. It is a future issue to associate these

distributions of chemical compositions with the actual aquifer distribution and paleo-environment and identify the cause of the characteristic distribution of chemical compositions, for the purposes of appropriate groundwater development and management.

5. Conclusions

The aquifers of the MRD are briefly classified into 2 aquifer units by the boundary at depth of 200 m. A wide variety of ion compositions and trace elements were found in the upper aquifer than the lower aquifer, and concentrations of some trace elements in groundwater were high and exceeding the WHO drinking water guideline values. The results indicate that groundwater in the upper aquifer is complex and the variety is assumed to be occurred by some reasons such as difference of recharge area, groundwater flow system, and multiple aquifer units. The result of PCA analysis shows that the groundwater quality along the MR and BR is dominated by high Na-Cl concentration type and other types ((Na+Mg)-HCO₃ and Na-HCO₃ types). The result of PCA analysis suggests that groundwater in the MRD originates from seawater and freshwater sources of the aquifer. High arsenic concentration was distributed in the upstream areas of the MRD. While the high concentration was rarely seen in the downstream areas of the MR and BR, the concentration exceeding the WHO guideline value was found on the left bank of the downstream areas. However, it is worth noting that the overexploitation and uncontrolled drilling of the aquifers for new deep wells in the downstream areas could increase a risk of arsenic contamination in deep groundwater.

Acknowledgements

This research was supported by JFGE (Japan Fund for Global Environment) and NIA (Niigata International Association). The

authors would like to acknowledge the Niigata Prefectural Institute of Public Health and Environmental Sciences and Fukushima Medical Device Development Support Centre, Japan for analysis of trace elements. This study was partially supported by the Nafosted Vietnam Project (105.03-2018.12).

References

- AAN and Research Group for Groundwater Contamination by Arsenic in the Mekong River Delta (Mekong Group), 2012. Groundwater arsenic contamination in the Mekong River Delta. The Association for the Geological Collaboration in Japan (AGCJ), 151pp. (in Japanese, English and Vietnamese)
- Appelo C.A.J., Postma D., 2005. Geochemistry, groundwater and pollution (2nd ed.). Rotterdam: A.A.Balkema Publishers, 649pp.
- Berg M., Stengel C., Pham T.K.T., Pham H.V., Sampson M.L., Leng M., Samreth S. and Fredericks D., 2007. Magnitude of arsenic pollution in the Mekong and Red River Deltas-Cambodia and Vietnam. *Science of the Total Environment*, 372, 413–425.
- Buschmann J., Berg M., Stengel C., Winkel L., Sampson M.L., Pham T.K.T., Pham H.V., 2008. Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population. *Environment International*, 34, 756–764.
- Erbas L.E., Gorelick S.M., Zebker H.A., Fendorf S., 2013. Release of arsenic to deep groundwater in the Mekong Delta, Vietnam, linked to pumping induced land subsidence. *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, 110, 13751–13756.
- Fabrice G.R., Claudia K., 2012. *The Mekong Delta System Interdisciplinary Analyses of a River Delta*. Springer Environmental Science and Engineering, Springer Netherlands, 463pp.
- General Statistics Office of Vietnam (GSO), 2016. Population and Employment, Statistical Yearbook of Vietnam 2015. Statistical Documentation and Service Centre General Statistics office of Vietnam,

- https://www.gso.gov.vn/Default_en.aspx?tabid=766, (Access, 2018/9/6).
- Hironaka H., 1998. On site analysis of As³⁺ and As⁵⁺ by mercury bromide paper disk colorimetry method (Gutzeit method modified by Hironaka). Annual Report of Fukuoka City Institute for Hygiene and Environment, 23, 120–122. (in Japanese with English abstract)
- Hoang T.H., Bäumle R., 2019. Complex hydrochemical characteristics of the Middle-Upper Pleistocene aquifer in Soc Trang Province, Southern Vietnam. Environmental Geochemistry and Health, 41, 325–341.
- Hoang T.H., Bang S., Kim K-W., Nguyen M.H., Dang D.M., 2010. Arsenic in groundwater and sediment in the Mekong River delta, Vietnam. Environmental Pollution, 158, 2648–2658.
- Ito T., Sato H., Shibasaki N., 2016. Groundwater arsenic and extent of contamination along the Mekong River, Vietnam. Arsenic Research and Global Sustainability (As2016), CRC Press, 70–71.
- Merola R.B., Hien T.T., Quyen D.T.T., Vengosh A., 2015. Arsenic exposure to drinking water in the Mekong Delta. Science of the Total Environment, 511, 544–552.
- Minderhoud P.S.J., Erkens G., Pham V.H., Bui V.T., Erban L., Kooi H., Stouthamer E., 2017. Impacts of 25 years of groundwater extraction on subsidence in the Mekong delta, Vietnam. Environmental Research Letters, 12, 064006.
- Ministry of Health, 2009. National technical regulations on drinking and domestic water quality. Report nr, 04/2009/TT-BYT, Hanoi, Vietnam. Socialist Republic of Vietnam. Ministry of Health General Department of Preventive Medicine & Environment, 9pp.
- Nguyen K.P., Itoi R., 2009. Source and release mechanism of arsenic in aquifers of the Mekong Delta, Vietnam. Journal of Contaminant Hydrology, 103, 58–69.
- Nguyen V.L., Ta T.K.O., Nguyen V.D., 2008. Recent situation of arsenic contamination in groundwater in Dong Thap province and its countermeasures. Technical Report, 98pp.
- Nguyen V.L., Ta T.K.O., Tateishi M., 2000. Late Holocene depositional environments and coastal evolution of the Mekong River Delta, Southern Vietnam. Journal of Asian Earth Sciences, 18, 427–439.
- Nickson R.T., McArthur J.M., Ravenscroft P., Burgess W.G., Ahmed K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry, 15, 403–413.
- Shinkai Y., Truc D.V., Sumi D., Canh D., Kumagai Y., 2007. Arsenic and other Metal Contamination of Groundwater in the Mekong River Delta Vietnam. Journal of Health Science, 53, 344–346.
- Tran D.A., Tsujimura M., Vo L.P., Kawauchi A., Doan T.H., 2014a. Chemical Characteristics of Surface Water and Groundwater in Coastal Watershed, Mekong Delta, Vietnam. The 4th International Conference on Sustainable Future for Human Security, SustaiN 2013. Procedia Environmental Science, 20, 712–721.
- Tran D.A., Tsujimura M., Vo L.P., Truong T.H., 2014b. Groundwater Flow System in Coastal Region of the Mekong Delta as Determined by Hydrogeochemistry. Proceeding of the 19th IAHR-APD Congress 2014, Hanoi, Vietnam ISBN 978604821338-1, 7pp.
- Wilkie J.A., Hering J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloids and Surfaces, 107, 97–110.
- World Health Organization, 2011. Guidelines for Drinking-water Quality Fourth Edition, 541pp.