CHAPTER IV

RESULTS

4.1 Field investigation

4.1.1 Field analysis of shallow groundwater samples

Field analyses are usually carried out for parameters like pH, EC and Eh which are measured directly by electrode in a flow through cell (Appelo & Postma, 2005). Moreover, the total dissolved solids were determined from the conductivity of the water samples.

In the dry season, the majority of this groundwater system is acidic, which the pH value ranges between 4.84 and 7.60 with a mean pH value of 5.95. The electric conductivity (EC) is between 72.20 μ S/cm and 1,601.00 μ S/cm with a mean of 505.52 μ S/cm. The oxidation reduction potential (ORP) on this season is between 37.80 mV and 489.90 mV with a mean value of 364.22 mV. The total dissolved solids in groundwater range from 50.54 mV and 1,120.70 mV with a mean of 353.87 mV as shown in Table 4.2.

In the rainy season, the majority of this groundwater system is acidic which the pH value ranges between 4.68 and 6.72 with a mean pH value of 5.72. The electric conductivity (EC) is between 85.60 μ S/cm and 1,964.00 μ S/cm with a mean of 476.35 μ S/cm. The oxidation reduction potential (ORP) on this season is between -102.80 mV and 258.00 mV with a mean value of 143.59 mV. The total dissolved solids in groundwater range from 59.92 mV and 1,374.80 mV with a mean of 333.45 mV as shown in Table 4.2.



4.1.2 The direction of groundwater flow

The groundwater levels were measured to determine the groundwater flow direction. The data were used to construct water level that is the groundwater level elevation as measured in shallow groundwater wells. The maximum groundwater level were 136.12 m and 139.32 m and minimum groundwater level were 15.81 m and 16.59 m (compared above mean sea level, msl) in dry and rainy season, respectively, as shown in Table 4.1.

The direction of horizontal groundwater flow can be inferred from maps of groundwater level altitude contours. The horizontal groundwater flow generally is in the direction of decreasing groundwater level altitudes and perpendicular to the groundwater level altitude contours. Groundwater level altitude maps were used to determine shallow groundwater flow directions and gradients as shown in Figure 4.1 and 4.2

		Water table (m, MSL)			
Well No.	UTM_E	UTM_N	Dry season	Rainy season	
TB001	718786	1446325	49.35	50.13	
TB002	718189	1445795	49.53	50.02	
TB003	717149	1445726	37.92	38.41	
TB004	717541	1447176	36.98	38.22	
TB005	716301	1447283	35.89	36.59	
TB006	721460	1444743	99.86	99.95	
TB007	719964	1445605	66.55	66.60	
TB008	720762	1446586	59.95	59.88	
TB009	722667	1445826	80.39	80.43	
TB010	724543	1449065	136.12	136.32	
TB011	717131	1443338	42.54	43.59	
TB012	715614	1444168	29.11	30.01	
TB013	714240	1444422	23.66	24.70	
TB014	713341	1443019	15.81	16.59	
TB015	715282	1445903	31.82	31.05	
TB016	720713	1444644	97.71	97.78	

Table 4.1 Location and groundwater levels from shallow groundwater wells



Figure 4.1 Groundwater level contour map in dry season



Figure 4.2 Groundwater level contour map in rainy season

4.2 Hydrochemical analysis

4.2.1 Hydrochemical properties of shallow groundwater

4.2.1.1 Hydrochemical analysis of shallow groundwater

The chemical analysis of groundwater standard was composed of at least four major cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) and four major anions (Cl⁺, HCO₃⁻, $SO_4^{2^{-1}}$ and NO_3^{-}) (Appelo, 2005). Enhancement of heavy metal concentrations constitutes a serious problem for water supply, once released to groundwater. The concentrations of As, Al, Cd, Fe, Pb, Mn and Zn were considered the quality of groundwater.

The water quality parameters in shallow groundwater wells were analyzed and reported as statistical results as shown in Tables 4.2 and 4.3 along with dry and rainy seasons, respectively. The Table shows the minimum, maximum, mean values and also standard deviation as well as maximum admissible concentrations (MAC) for drinking water, which is maximum acceptable concentrations of heavy metals that adversely affect to human health,

In dry season, ranges of cation concentrations of Ca^{2+} , Mg^{2+} . Na^{+} and K^{+} varied from 0.93 to 70.50 mg/L, 0.25 to 24.58 mg/L, 1.95 to 261.40 mg/L and 1.49 to 18.25 mg/L and mean values are 16.22, 4.98, 35.03 and 5.18 mg/l, respectively. For the anions, concentrations of HCO_{3}^{-} , Cl^{-} , SO_{4}^{-2} and NO_{3}^{--} are between 8.00 to 430.00 mg/L, 1.07 to 19.06 mg/L, 34.80 to 79.20 mg/L and 1.49 to 63.29 mg/L with mean values of 105.33, 4.87, 54.20 and 21.93 mg/L, respectively.

In rainy season, ranges of cation concentrations of Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} varied from 0.01 to 17.98 mg/L, 0.05 to 10.39 mg/L, 0.21 to 62.66 mg/L and 0.52 to 72.25 mg/L, with mean values of 7.48, 2.61, 10.86 and 7.89 mg/L, respectively. For the anions, HCO_{3}^{-} , Cl^{-} , SO_{4}^{2-} and NO_{3}^{-} concentrations are between 12.00 to 1,128.00

mg/L, 8.86 to 1,380.00 mg/L, 0.98 to 175.00 mg/L and 0.31 to 54.15 mg/L with mean values of 187.78, 123.40, 35.49 and 16.16 mg/L, respectively.

Chemical constituents			S	itatistics	
(mg/L)	*MAC	Min	Max	Mean	SD
pH (Unit)	6.5-8.5	4.84	7.60	5.95	0.72
EC (µS/cm)	-	72.20	1,601.00	505.52	398.09
ORP (mV)	-	37.80	489.90	364.22	116.30
TDS	-	50. 5 4	1,120.70	353.87	278.66
Ca ²⁺	-	0.93	70.50	16.22	17.14
Mg ²	50	0.25	24.58	4.98	5.93
Na ⁺	200	1.95	261.40	35.C3	62.78
K	-	1.49	18.25	5.18	4.71
HCO3	-	8.00	430.00	105.33	122.63
CL	250	1.07	19.06	4.87	4.76
SO42-	250	34.80	79.20	54.20	12.39
NO ₃	-	1.49	63.29	21.93	18.81

Table 4.2 The statistics of groundwater quality in shallow groundwater wells in dry season

Table 4.3 The statistics of groundwater quality in shallow groundwater wells in rainy season

Chemical constituents		Statistics				
(mg/L)	*MAC	Min	Max	Mean	SD	
pH (Unit)	6.5-8.5	4.68	6.72	5.72	0.62	
EC (µS/cm)	-	85.60	1,964.00	476.35	428.27	
ORP (mV)	-	-102.80	258.00	143.59	98.09	
TDS	-	59.92	1,374.80	333.45	299.79	
Ca ²⁺	-	0.01	17.98	7.48	5.76	
Mg ²⁺	50	0.05	10.39	2.61	3.01	
	200	0.21	62.66	10.86	14.20	
K	-	0.52	72.25	7.89	17.52	
HCO ₃	-	12.00	1,128.00	187.78	303.77	
Cl	250	8.86	1,380.00	123.40	315.92	
SO42-	250	0.98	175.00	35.49	37.39	
NO ₃	-	0.31	54.15	16.16	17.28	

*MAC= Maximal admissible concentration (mg/L).

The results of heavy metals were reported as shown in Tables 4.4 and 4.5 in dry and rainy seasons. The concentration of Zn ranges from 0.008 to 0.406 mg/L with the mean Zn of 0.046 mg/L, which were lower than MAC. Also, the concentration of As is maximum of 0.107 mg/L. Iron, Mn and Al are 0.011 to 7.295 mg/L, 0.001 to 2.061 mg/L and 1.111 to 0.213 mg/L, mean values of 1.065, 0.397 and 0.213 mg/L respectively, exceeding the acceptable limit for drinking purpose.

In rainy season, concentrations of Zn and Al are 0.002 to 0.025 mg/L and 0.001 to 0.142 mg/L, a mean value of 0.015 and 0.047 mg/L, which are lower than the maximum admissible concentration. The maximum concentration of As in this season is approx. 0.013 mg/L. Also, ranges of Fe and Mn varied from 0.002 to 3.584 mg/L and 0.002 to 0.733 mg/L, with average values are 0.624 and 0.282 mg/L, respectively, which exceed the acceptable limit for drinking purpose. Location of groundwater wells found amounts of As, Fe, Mn and Al exceeding groundwater quality standard shows in Figure 4.3 to 4.9.

Chemical constituents			St	atistics	
(mg/L)	MAC	Min	Max	Mean	SD
As	0.01	0.0004	0.107	0.009	0.027
Fe	0.30	0.011	7.295	1.065	1.704
Mn	0.05	0.001	2.061	0.397	0.592
Zn	5.00	0.008	0.406	0.046	0.092
Al	0.20	0.002	1.111	0.213	0.386

Table 4.4 The statistics of groundwater quality in shallow groundwater wells in dry season

Table 4.5 The statistics of groundwater quality in shallow groundwater wells in rainy season

Chemical constituents					
(mg/L)	MAC	Min	Max	Mean	SD
As	0.01	ND	0.013	ND	ND
Fe	0.30	0.002	3.584	0.701	1.203
Mn	0.05	0.002	0.733	0.212	0.259
Zn	5.00	0.002	0.025	0.015	0.019
Al	0.20	0.001	0.142	0.047	0.051







Figure 4.3 Well locations of As exceeding over groundwater quality standard in dry season

Figure 4.4 Well locations of As exceeding over groundwater quality standard in rainy season







Figure 4.5 Well locations of Fe exceeding over groundwater quality standard in dry season

Figure 4.6 Well locations of Fe exceeding over groundwater quality standard in rainy season





Figure 4.7 Well locations of Mn exceeding over groundwater quality standard in dry season

Figure 4.8 Well locations of Mn exceeding over groundwater quality standard in rainy season



Figure 4.9 Well locations of Al exceeding over groundwater quality standard in dry season

4.2.1.2 Groundwater types

Piper diagram is widely used for representation of chemical characteristics of groundwater samples (Li et al., 2013). The piper diagram contains two triangle charts, one for plotting cations in the left conner and the other for plotting anions in the right conner. The two data points in the triagles are combined by drawing line parallel to the diamond shape. The relative hydrochemical composition of the groundwater samples are indicated by a single point (Appelo & Postma, 2005).

In dry season, the cation composition mostly falls within sodium or potassium type. There are some that fall within the regions of no dominant type and calcium type. According to anion composition, sulfate type is mostly represented. Therefore, the facies name would be mixed type which can be seen in Figure 4.10.

In the rainy season, the water samples mostly are fallen within the region of sodium or potassium type, some are in no dominant and calcium region. For the anion composition, bicarbonate type, no dominant type and chloride type are represented. Therefore, the facies name would be calcium-bicarbonate type, sodium-chloride type and mixed type as shown in Figure 4.11.



Figure 4.10 Piper diagram of shallow groundwater samples in dry season



Figure 4.11 Piper diagram of shallow groundwater samples in rainy season

4.2.1.3 Arsenic speciation

Arsenic is considered to be toxic element, even in low concentration (Mayer, Kosmus, Pogglitsch, Mayer, & Beyer, 1993). In aqueous environment, As generally presents as arsenite (As^{+3}) and arsenate (As^{+5}) . Arsenic metal rarely occurs and oxidation state -3 is found only in high reduction environment. The aqueous stability of arsenic compounds is influenced by the pH value and the redox potential (ORP), which can be presented in the Eh-pH diagram (Stollenwerk & Welch, 2003).

In the dry season, the pH values were 4.84 to 7.60 and ORP values were between 37.80 and 489.90 mV. The results have found that pH–Eh data plot completely in As^{+5} as shown in Figure 4.12.

In the rainy season, the pH values were between 4.68 to 6.72 and ORP were between -102.80 and 258.00 mV. The results also have found that pH–Eh data plot completely in As^{+5} as shown in Figure 4.13.





Figure 4.12 The Eh-pH diagram of arsenic speciations in dry season



Figure 4.13 The Eh-pH diagram of arsenic speciations in rainy season

4.2.2 Physico-chemical properties of soils

4.2.2.1 Soil texture

Sieve analysis is used to separate particles size and determined quantitatively the mass of particles in each range. The results of sieve analysis are the percentage of the total weight of soil that passed through different number of sieves (see Table 4.6). Figure 4.14 shows particle size distribution curve.

The textural triangle is used to determine soil types, based on percentage of sand, silt and clay which is determined from laboratory analysis (Gradiner and Miller, 2001). The texture of soil can divided into 3 groups as follow: 1) sandy loam, 2) loamy sand and 3) sand, respectively as shown in Figure 4.15.

Soil Group	% Sand	% Silt	% Clay
Group 1	76.0	8.8	15.2
Group 2	84.2	6.4	9.4
Group 3	92.0	2.6	5.4

Table 4.6 The percentage of sand, silt and clay in each soil group



Figure 4.14 The partical size distribution curve of soil





(Credit : United State Department of Agriculture)



4.2.2.2 The chemical properties of soil

The chemical properties of soils including pH, electrical conductivity (EC), cation exchange capacity (CEC), organic matter (OM) and concentrations of K^{*} , Na^{*}, Ca²⁺, Mg²⁺, Fe and Mn are showed in Table 4.7.

Paramotor	Linit	Sample No.				
Falameter	Onit	Sandy loam	Loamy sand	Sand		
рН	_	5.20	5.30	5.40		
EC	dS/m	0.02	0.02	0.01		
OM	%	0.13	0.13	0.13		
CEC	cmol/kg	6.00	1.30	1.40		
K⁺	mg/kg	81.00	24.00	11.00		
Na ⁺	mg/kg	23.00	11.00	15.00		
Ca ²⁺	mg/kg	457.00	147.00	65.00		
Mg ²⁺	mg/kg	199.00	19.00	13.00		
Fetot	mg/kg	5.00	3.05	17.47		
Mn	mg/kg	18.78	13.62	7.83		

Table 4.7 Summary of the chemical properties of soil

4.2.2.3 The chemical compositions of soil

X-ray fluorescence (XRF) is a technique to determine the element composition. The data in the Table 4.8 shows that the silica and alumina oxide are presented in the major quantities, while the other mineral are presented in trace amounts, in all the three soils.

X-ray diffection (XRD) is used to determine the mineralogical composition in the qualitative and quantitative phase of the material components (Nayak & Sigsh, 2007). The characterization of XRD patterns indicates that quartz as the major phases, in all of three soils (Figure 4.16).

	Weight (%)					
Constituents –	Sandy loam	Loamy sand	Sand			
SiO ₂	73.60 %	91.30 %	93.60 %			
Al ₂ O ₃	15.40 %	5.72 %	4.07 %			
K ₂ O	6.32 %	1.13 %	1.19 %			
Fe ₂ O ₃	2.35 %	1.00 %	0.61 %			
TiO ₂	0.59 %	0.47 %	0.26 %			
Na ₂ O	0.54 %	ND	ND			
MgO	0.51 %	ND	ND			
CaO	0.18 %	ND	ND			
BaO	0.14 %	ND	ND			

Table 4.8 The chemical composition of soil in the study area by the X-ray fluorescence (XRF)







The point of zero charge (PZC) is the pH value, which the net total particles charge is zero. The PZC results of sand and sandy loam are pH values of 4.80 ± 0.5 and 4.28 ± 0.25 , respectively (Figure 4.17).



Figure 4.17 Point of zero charge for (a) sand and (b) sandy loam



4.3 The column experiments and modeling

The two columns (sand and sandy loam) were packed by the wet packing technique. The physical characteristics of soil medias used in column experiments are shown in Table 4.9.

Parameter	Unit Column No.1		Column No.2
		Sandy loam	Sandy
Bulk density (BD)	g/cm ³	1.35	1.59
Porosity (n)	(-)	0.44	0.30
Pore volume (PV)	cm ³	21.59	14.72
Seepage velocity (Ks)	cm/hr	4.55	6.67

Table 4.9 Physical characteristic of soil in column transport experiments

4.3.1 Dispersion coefficient of soil

NaBr was used to be the non-reactive in this experiment. The HYDRUS-1D model was used to fit the observed data effluent bromide concentrations. According to breakthrough curves (BTCs) expressed the relative between normalized concentration (C/C_0) versus pore volume (PV) of experimental and simulated breakthrough curve (BTC) shown in Figure 4.18. The results found that the dispersion coefficients of sand and sandy loam are 18.68 and 13.65 cm³/hr, respectively.



Figure 4.18 Experimental and simulated breakthrough curves (BTCs) of Br⁻ in sandy loam and sand

4.3.2 Arsenic transport

Figure 4.19 displays concentrations of As with pore volume (PV) derived from column experiments. The experiment results were then input to fitted by using HYDRUS-1D. The results found that Freundlich isotherm was used to well explain the arsenic sorption coefficient in soil. Table 4.10 contains the input parameters, which consist of bulk density, longitudinal dispersivity (Smedley & Kinniburgh), sorption isotherm coefficient Nu (η) and Beta (β). The sorption coefficient of sandy loam and sand ranges from 20 cm³/mg and 6-8 cm³/mg, respectively (Figure 4.20).

Table 4.10 The soil specific parameters, solute transport and reaction parameters forHYDRUS-1D

Sample	Bulk density (g/cm³)	Longitudinal dispersivity** (cm)	Kd* (cm ³ /mg)	Nu* (η)	Beta* (eta)
Sandy loam	1.35	3	20	0	0.5
Sandy	1.59	2.8	6 - 8	0	0.5

* The results derived from fitting by HYDRUS-1D

** The results derived from tacer test





Figure 4.19 Experimental breakthrough curves of arsenic versus pore volume (PV) (a) sandy loam and (b) sand





Figure 4.20 Experimental and simulated breakthrough curves of arsenic versus time fitted by HYDRUS-1D: (a) sandy loam and (b) sand

4.3.3 The distribution of total As concentration in soils

The distribution of total arsenic concentration in soils were analyzed by soil microwave digestion method (followed EPA 3015A). The soil samples were collected after As transport experiments were completed and divided into 10 sections.





Figure 4.21 As distribution profile in soil: (a) sandy loam and (b) sand



Figure 4.22 Comparison of As distribution in sandy loam and sand

The results were presented in Figure 4.21. The inlet of As solution was at depth 1 cm, thus the concentrations of As were high and decreased with distance. The comparing of As distribution between sandy loam and sand were shown in Figure 4.22. Moreover, the results given in Table 4.11 were reported the sorption capacity of arsenic transport through saturated soil. Arsenic was sorbed in sandy loam more than that in sand.

	Initial	Weight	As	As	04	Serbed	Sorption
Sample	conc. Of	of soil	(Influent)	(Effluent)	70		capacity
	As (ppm)	(g)	(mg)	(mg)	recovery	As (mg)	(mg/g)
Sandy loam	3.11	66.45	2.01	0.08	96.22	1.46	0.021
Sandy	3.40	78.44	2.33	1.39	40.49	0.31	0.004

Table 4.11 Sorption capacity of arsenic transport through saturated soil

4.4 Groundwater flow and arsenic transport modeling

4.4.1 Conceptual model

A conceptual model is a pictorial representation of the groundwater flow system, which consists of the basic components such as the source of water, the topography and physical boundaries of the area and hydrogeological properties. It is frequently in the form of cross-section (Anderson & Woessner, 1992). According to the result of groundwater level measurement, groundwater flows in this area are flow from the northeast to the southwest (Figure 4.23). The hydrogeological setting of this area is in unconsolidated sand and gravel aquifer as the cross-section (Figure 4.24).



Figure 4.23 Map shown shallow groundwater flow in the study area.



Figure 4.24 The geological cross-section of study area

(data derived from Department of Groundwater Resources (DGR), 2010)

4.4.2 Steady-state calibration

The results of steady-state calibration in the study area, sixteen observation wells were used to compare with simulated groundwater heads. After parameter estimation, it found that the simulated groundwater heads were corresponded with observed groundwater heads as shown in Figures 4.25 and 26 and Tables 4.12 to 4.13. The scatter plot shows the relationship of simulated groundwater heads and sampling wells along the linear diagonal line.

In the dry season, the residual mean of the water level after adjusting is -0.39 meters. The absolute residual mean of the water level after adjusting is 1.16 meters. And the root mean squared is 1.52 meters with the maximum permissible error of 1.27.

In the rainy season, the residual mean of the water level after adjusting is 0.29 meters. The absolute residual mean of the water level after adjusting is 1.03 meters. And the root mean squared is 1.38 meters with the maximum permissible error 1.15.

An indication of modeling is reliability because the maximum permissible error should not over than 5%.



Figure 4.25 Scattered plot between simulated and observed heads of steady-state condition (a) dry season and (b) rainy season

Observed



Figure 4.26 Simulated groundwater head under steady-state condition in (a) dry season and (b) rainy season

Descriptions	Value (m)
Mean Residual (Head)	-0.39
Mean Absolute Residual (Head)	1.16
Root Mean Squared Residual (Head)	1.52
Mean Weighted Residual (Head+Flow)	-0.76
Mean Absolute Weighted Residual (Head+Flow)	2.26
Root Mean Squared Weighted Residual (Head+Flow)	2.97
Sum of Squared Weighted Residual (Head+Flow)	70.60

Table 4.12 Residual analysis of the steady-state condition in the dry season

Table 4.13 Residual analysis of the steady-state condition in the rainy season

Descriptions	Value (m)
Mean Residual (Head)	0.29
Mean Absolute Residual (Head)	1.03
Root Mean Squared Residual (Head)	1.38
Mean Weighted Residual (Head+Flow)	0.57
Mean Absolute Weighted Residual (Head+Flow)	2.01
Root Mean Squared Weighted Residual (Head+Flow)	2.70
Sum of Squared Weighted Residual (Head+Flow)	58.39

4.4.3 Modeling of As transport

Mass transport has been investigated and simulated by using MT3D, which is a computer model for simulation of advection, dispersion and chemical reactions of soluble contaminants in three-dimensional groundwater flow systems.

Concentration of As 0.25 mg/L was used as initial concentration parameter which this value was reported by The Laem Chabang Municipality, Sriracha, Changwat Chonburi. The As transport was simulated in 3 periods including 15 years (2010 – 2025), 25 years (2010 - 2035) and 50 years (2010 - 2060).

According to the Figure 4.27, comparing As transport in difference soil type between sand and sandy loam at 15 years, depending on their sorption. The results showed that As was slowly spreaded from the source and moved though sand aquifer better than that in sandy loam, also with time of 25 years and 50 year as shown in Figures 4.28 and 4.29, respectively. In worst case scenario no sorption, the Figure 4.30 showed that As was rapidly movement.

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Figure 4.27 Arsenic movement of 15 years during 2010 - 2025

(a) sand and (b) sandy loam







Figure 4.28 Arsenic movement of 25 years during 2010 - 2035

(a) sand and (b) sandy loam





Figure 4.29 Arsenic movement of 50 years during 2010 - 2060 (a) sand and (b) sandy loam







(a) 15 years, (b) 25 yesrs and (c) 50 years



Figure 4.31 Arsenic movement without the sorption (a) 15 years, (b) 25 yesrs and (c) 50 years (continue)