

CHAPTER II

THEORY AND LITERATURE REVIEWS

Two major topics will be presented: a) the theoretical background, including groundwater flow, groundwater contamination and transports, modeling of groundwater and arsenic in groundwater and b) the previous investigations for contamination of arsenic in groundwater.

2.1 Theoretical background

2.1.1 Groundwater flow

Darcy's law

In 1856 Henry Darcy, a French engineer, investigated the flow of water through horizontal beds of sand by using water filtration. According to the investigation, it was found that the flow rate (Q) is proportional to cross sectional area (A) and the piezometer high difference (Δh) moreover, inversely proportional to distance (L) (Figure 2.1).

The Darcy's measurements showed the proportionalities

$$Q \propto h_a - h_b \quad \text{and} \quad Q \propto \frac{1}{L} \quad 2.1$$

Expressed in general terms

$$Q = -KA \left(\frac{dh}{dL} \right) \quad 2.2$$

or simply

$$V = \frac{Q}{A} = -K \left(\frac{dh}{dL} \right) \quad 2.3$$

where V is the Darcy velocity or specific discharge, the negative sign is a flow of water in the direction of decreasing head. K , the proportionality constant is called the hydraulic conductivity which related to the size and tortuosity of the pores. (Fetter, 2001)

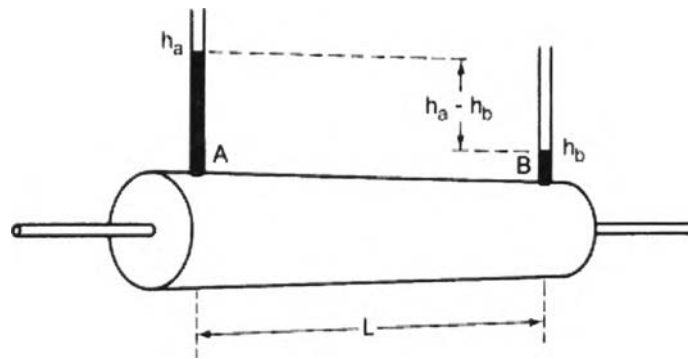


Figure 2.1 Darcy's experiment (Fetter, 2001)

The velocity V in equation 2.3 is referred to as the *Darcy velocity*. It assumes that flow occurs through the entire cross-section of the material without consideration of solids and pores.

Therefore, the seepage velocity or average linear velocity is the result of velocity, which actually, water flow is limited only to the pore space.

$$V_x = \frac{Q}{n_e A} = -\frac{Kdh}{ndl} \quad 2.4$$

where V_x is the average linear velocity (L/T)

n_e is the effective porosity

Darcy's Law is valid for laminar flow at very low velocities, thus it can apply in the most situations of ground water flow through porous media due to generally groundwater transfer very slowly (typically up to 1 m/day). If flows are turbulent flow and high velocities, specific discharge would not be proportional to the hydraulic head gradient, such as in flow through very large fractures or near very high pumping wells Darcy's Law is not available.

2.1.2 Mass transport of solutes

There are three processes:

1. **Advection** is the process by which moving groundwater carries with it dissolved solutes. The advection of contaminants change at the same rate with the average linear velocity of the groundwater. The rate of groundwater flow can be determined by Darcy's law as

$$V_x = -\frac{K}{n_e} \frac{dh}{dl} \quad 2.5$$

where V_x is average linear velocity, K is hydraulic conductivity, n_e is effective porosity and $\frac{dh}{dl}$ is hydraulic gradient.

2. Diffusion is the process by which both ionic and molecular species dissolved in the water move from areas of high concentration to area lower concentration. The diffusion equation can be described by Fick's first laws.

$$F = -D \frac{\partial c}{\partial x} \quad 2.6$$

where F is mass flux of solute (mg/s/cm^2), D is the diffusion coefficient (cm^2/s), C is the solute concentration (mg/cm^3) and $\frac{\partial c}{\partial x}$ is concentration gradient ($\text{mg/cm}^3/\text{cm}$).

In porous media, an effective diffusion coefficient must be used, termed D^* .

$$D^* = wD \quad 2.8$$

where w is an empirical coefficient that is determined by laboratory experiment.

(Fetter, 2001)

3. Dispersion is the process by which resulting in dilution of the contamination when the contaminated fluid mixes with non-contaminated groundwater. There are two types of dispersion; longitudinal dispersion (Smedley & Kinniburgh) has caused from difference in travel time along the flow line around grains whereas transverse dispersion occur normal to the pathway of fluid flow (Figure 2.2).



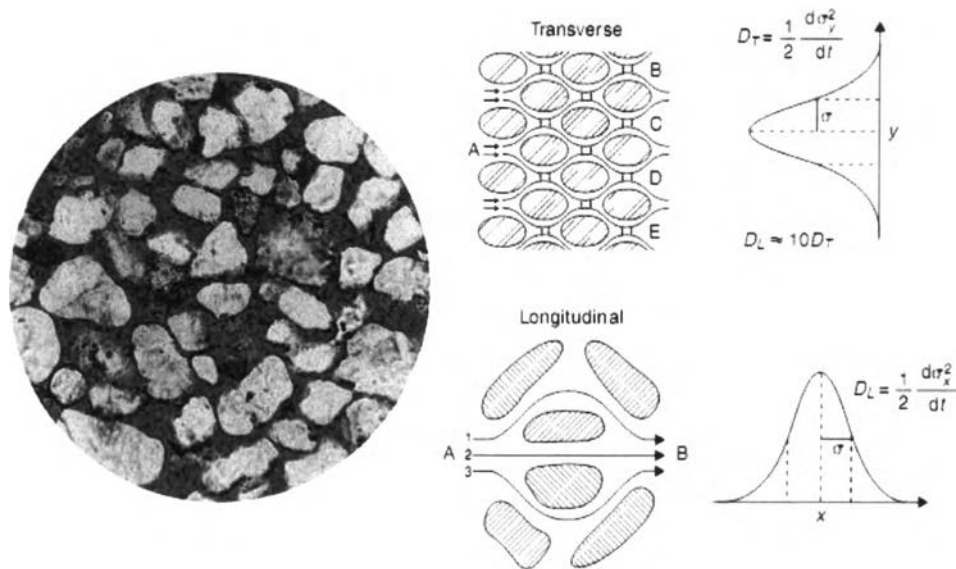


Figure 2.2 Longitudinal and transverse dispersion viewed at the microscopic scale

(Appelo & Postma, 2005)

In groundwater, the processes of diffusion and dispersion cannot be separated. The coefficient of hydrodynamic dispersion, D_L is used for a factor term. For one-dimensional flow the equation is represented as:

$$D_L = a_L v_x + D^* \quad 2.9$$

where D_L is the longitudinal coefficient of hydrodynamic dispersion, a_L is the dynamic dispersivity, v_x is the average linear ground-water velocity and D^* is the effective molecular diffusion coefficient.



2.1.3 Sorption Isotherms

The ability of a soil to adsorb a solute from solution can be determined in the laboratory. The difference between the initial and final concentration is the amount that was absorbed by the soil. Thus the mass adsorbed (S) in mg/g of dry soil can be calculated as:

$$S = \frac{(C_i - C)V}{S_m} \quad 2.10$$

where C_i is the initial concentration of adsorbate in mg/L, V is volume of solution in ml, S_m is a soil mass in g.

If the laboratory is using different values of absolute concentration in the solution, the relation between the amount of adsorbed and the equilibrium concentration at a constant temperature is a sorption isotherm (Kehew, 2001).

The most frequently used isotherms are Freundlich isotherm and the Langmuir isotherm. The Freundlich isotherm is defined by the equation

$$S = K_f C^n \quad 2.11$$

In which K_f is the partition coefficient and n are variables, a maximum value of 1.0 at that time the graph becomes linear. If n value is less than 1.0, the curve is concave with along to the concentration axis (Figure2.3). It is indicating that as the solution concentration increase, the amount of the adsorbed does not increase in proportion to the equilibrium concentration. A linear Freundlich isotherm ($n = 1$), K is called the distribution coefficient, K_d . The Freundlich isotherm can used for the sorption of hydrophobic organic but does not fit the adsorption of most inorganic solute.



The Langmuir isotherm fits the case that the sorption of the adsorbate approaches a maximum sorption capacity, S_{max} when all available surface sites are saturated. The equation of Langmuir isotherm is expressed as:

$$S = \frac{S_{max} KC}{1 + KC} \quad 2.12$$

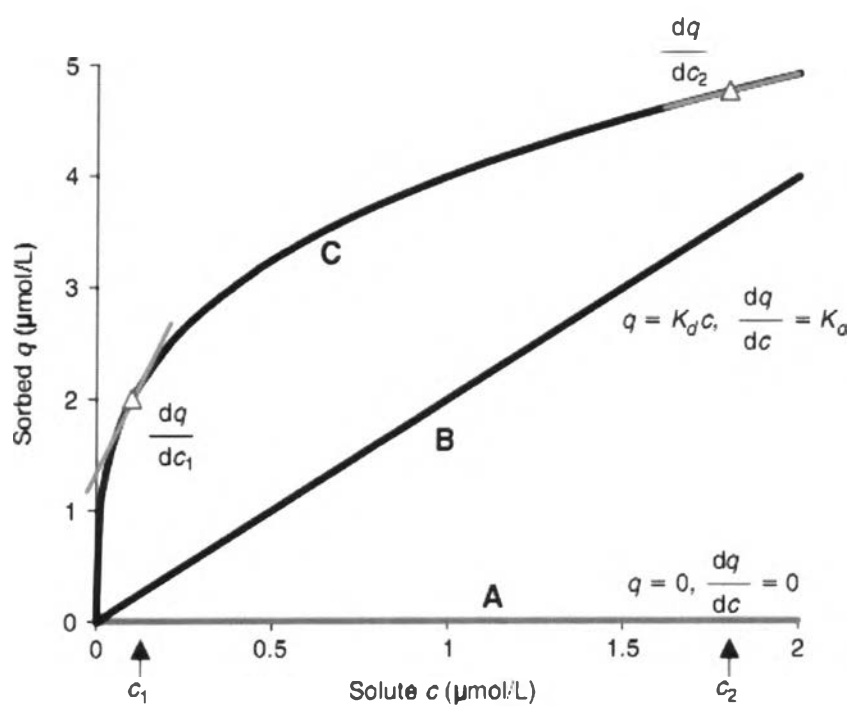


Figure 2.3 Examples of sorption isotherms: A: no sorption, B: Freundlich and C: Langmuir isotherms (Appelo & Postma, 2005)

2.1.4 Modeling of groundwater

Most groundwater modeling is proposed at predicting the consequences of the action. The model can be used for an interpretation which use as a framework for organizing field data in a dynamic system, moreover can also be used in the generic geologic setting. The step of modeling protocol is summarized in Figure 2.4.

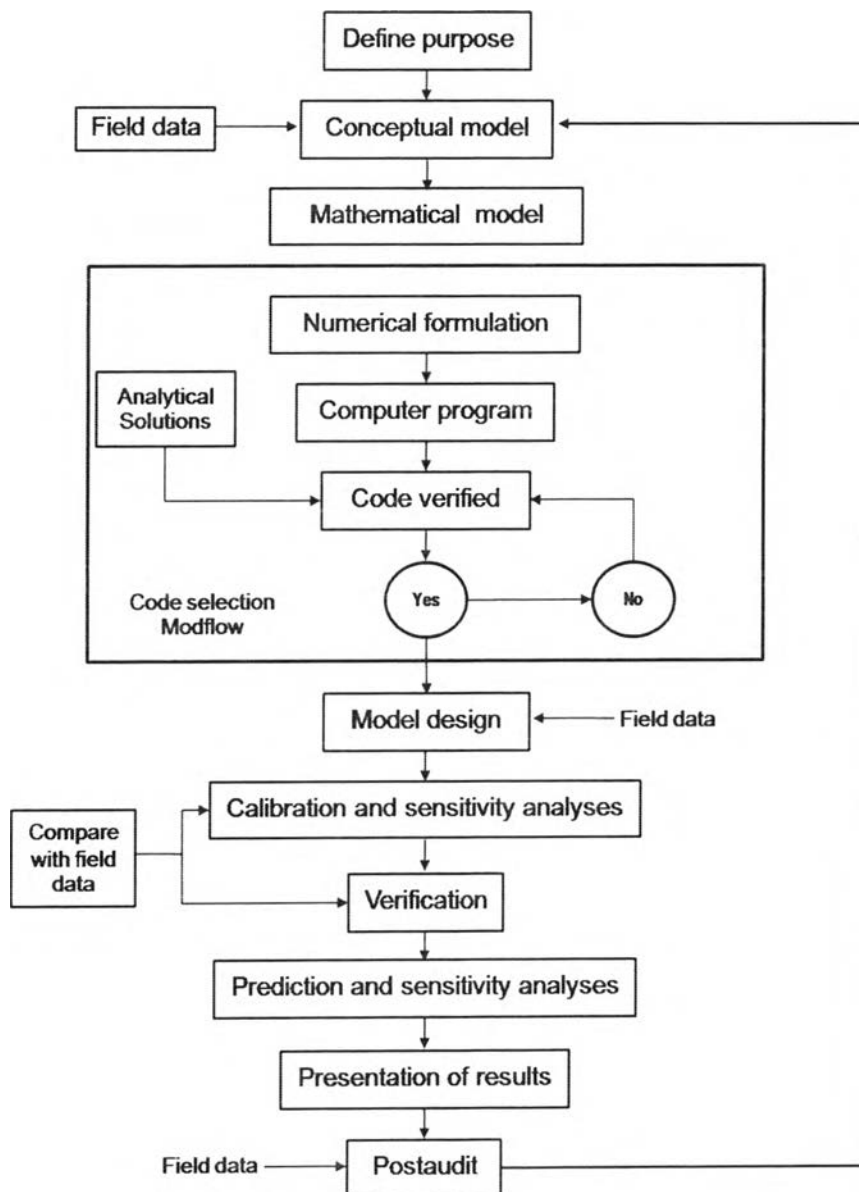


Figure 2.4 Step in a protocol for model application

(Anderson & Woessner, 1992)

Modflow Basics

Modflow is a block-centered finite-difference model. It can simulate confined, unconfined aquifers and leaky confined. It only simulates saturated flow in a porous medium with uniform temperature and density. It cannot simulate the multiphase flow such as flow in the unsaturated zone, flow in fractured zone, density-dependent flow or a varying anisotropy conditions in an aquifer (Fetter, 2001).

The Groundwater Modeling System (GMS) is a comprehensive graphical user environment for performing groundwater simulations. The entire GMS system consists of a graphical user interface (the GMS program) and a number of analysis codes (MODFLOW, MT3DMS, etc.). The GMS interface is developed by Aquaveo, LLC in Provo, Utah. GMS was designed as a comprehensive modeling environment. Several types of models are supported and facilities are provided to share information between different models and data types.

MT3DMS is a modular three-dimensional transport model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems (Zheng & Wang, 1999). MT3DMS uses a modular structure similar to the structure utilized by MODFLOW. MT3DMS is used in conjunction with MODFLOW in a two steps flow and transport simulation. Heads and cell-by-cell flux terms are computed by MODFLOW during the flow simulation.



2.1.5 Arsenic in groundwater

The long-term exposure to arsenic has various types of health impacts, including several types of cancer, cardiovascular disease, diabetes, and neurological effects (Council, 1999). To protect consumers served the public water from the effects of long-term exposure to arsenic, EPA has set the standard for drinking water of arsenic lowered the MCL (Maximum Concentration Limit) from 50 micrograms per liter ($\mu\text{g/L}$) to 10 $\mu\text{g/L}$ (Agency, 2001a; USEPA, 2001). The World Health Organization has set a provisional guideline concentration for drinking water of 10 $\mu\text{g/L}$ (WHO, 1993).

Dissolved Arsenic speciation is important in determining the extent of reaction with solid phase and the mobility of arsenic in groundwater. Arsenic is generally present as arsenate (As^{+5}) or arsenite (As^{+3}) for Eh condition prevalent in most groundwater (Figure 2.5). In strongly reducing environments, arsenic metal and arsine (As^{-3}) can exist. The both As^{+3} and As^{+5} form protonated oxyanions in aqueous solution, the degree of protonation depend on pH. As^{+3} is the dominant form under moderately reducing conditions. For a pH of common groundwater, As^{+3} species in solution are H_3AsO_3 up to pH 9.2 and H_2AsO_3^- from pH 9.2-12. For As^{+5} , is generally stable in oxidizing environments; the solution of H_2AsO_4^- predominates between pH 2.2 - 6.9 and HAsO_4^{2-} between pH 6.9 and 11.5 (Ferguson & Gavis, 1972).

The process that controls the partitioning of arsenic between aqueous and solid phases, including mineral precipitation/dissolution, adsorption/desorption, oxidation/ reduction and biological transformation, but the most significant process controlling arsenic concentration in groundwater is adsorption and desorption (Stollenwerk & Welch, 2003).



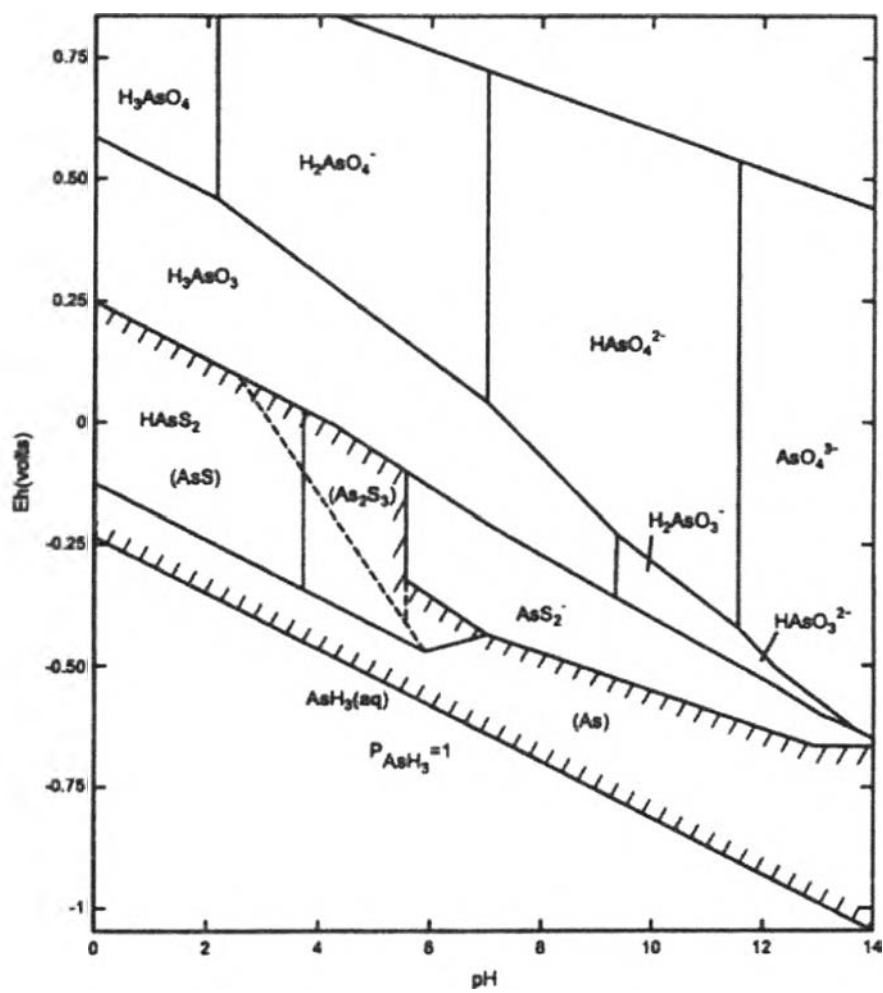


Figure 2.5 The Eh-pH diagram for As

(Ferguson & Gavis, 1972)

2.1.6 Piper diagram

Piper diagram is widely used for representation of chemical characteristics of groundwater samples (Li et al, 2013). The classification of water type based on the locations of plotting points in the ion triangles as Figure 2.6 (Kehew, 2001).

Piper diagrams show the relative concentrations of seven ions in solutions. The cations are Ca, Mg, Na and K. The anions are Cl, SO₄, and HCO₃. In most natural waters, there are these ions 95 to 100% of the ions in solution.

The Piper diagram includes two trilinear diagrams, one for anions and another one for cations. For each constituent, the concentration (mg/L) is converted to chemical equivalents (meq/L) based on the valence and atomic weight. Then the percentages of each ion relative to the total are calculated and plotted on the Piper diagram.

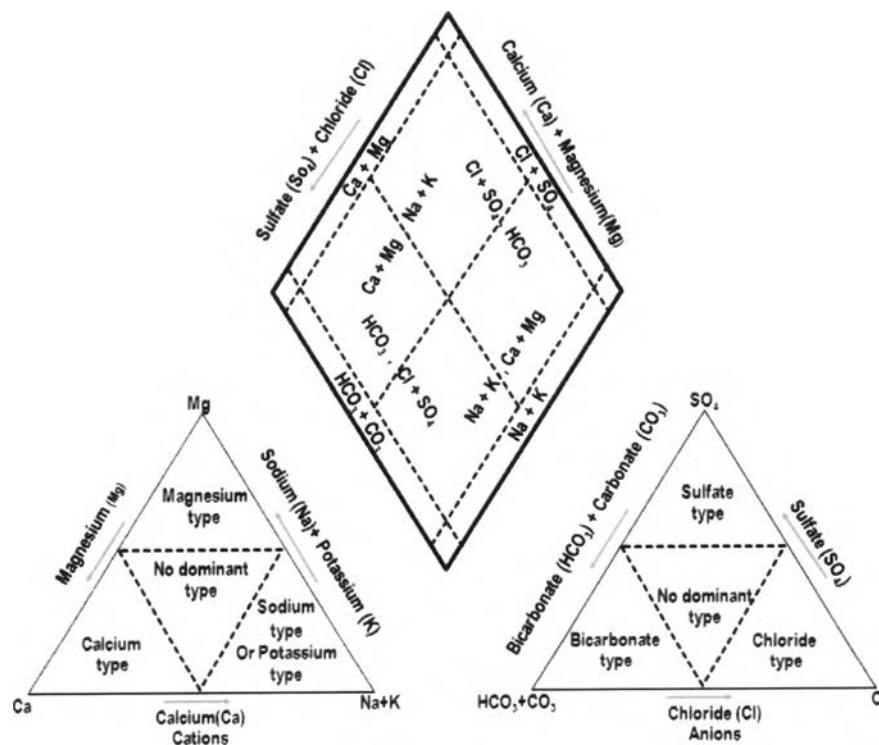


Figure 2.6 Classification of hydrochemical facies using the Piper plot

Figure adapted from Kehew, 2000

2.2 Previous investigation in contamination of arsenic in groundwater and the related investigation

The previous investigations of arsenic contamination in groundwater have been studied in many parts of the world and also have been used in many methods. Some of the important literatures have been briefly reviewed as the background information as below:


Ryu, Gao, Dahlgren, and Zierenberg (2002) have studied the spatial distribution of dissolved arsenic in the shallow groundwater and examined the factors affecting arsenic solubility and speciation. Owens Lake was the study area where located in southern California. It was an essentially dry lake with 280 km². Groundwater recharge occurs from direct precipitation, run off from the surrounding mountains, subsurface flow from the upper Owens Valley, and inflow from the Owens River. Therefore, evaporation is the major process which causes groundwater is lost. The samples were collected from the Great Basin Unified Air Pollution Control District (GBAPCD) piezometer network in fall 1992, spring 1993 and fall 1993. The result was found that dissolved arsenic concentrations ranged from 0.1 to 96 mg/L and generally increased from the shoreline to the center of the lakebed. Arsenic concentrations were strongly associated to electrical conductivity (EC) and δD . Arsenite (As^{+3}) was the dominant form at Eh values less than about -170 mV, while arsenate (As^{+5}) was predominant at higher Eh values. The solid-phase arsenic concentrations ranged between 4.0 and 42.6 mg/kg and a maximum concentration range was increased up to 80 mg/L. In the solid phase, only at high arsenic and sulfide concentrations were a positive saturation index with orpiment (As_2S_3).



Tan (2006) has investigated the leaching column tests on arsenic-soil interactions. An artificial soil was characterized its physical, chemical and mineralogical properties before leached the column test. Arsenate solution was prepared from reagent grad sodium arsenate (Na_2HAsO_4) in distilled de-ionized water of pH 7 with the concentration 250 ppm. The acrylic tube column was a length of 150 cm and an inner diameter of 75 cm. As the experiment, the leaching column tests were conducted for 4 columns (A to D) and the artificial soil was various proportions of organic topsoil (0, 2%, 5% and 10%). The soil column was first saturated by flushing 2 pore volumes of distilled water. After the saturation procedure, arsenic solution was injected for 8 pores and then leaching with distilled water for another additional 5 pore volumes. The results of experiment found that the organic matter has the effect with the adsorption and desorption of arsenic. A larger amount of organic matter will significantly increase the adsorption capability more than a small amount. Sivakumar and Elango (2007) have investigated the simulation of the groundwater contamination in the upper Palar River basin in Tamil Nadu. MODFLOW and MT3D were used to simulate the groundwater flow and transport. The simulation was done in the transient state for one year. For the migration of contamination plume, the important input for MT3D are the initial concentration of the effluent, porosity, stress period for transient condition, areal source/sink and longitudinal dispersivity.

Smith and Naidu (2009) have investigated the vertical distribution of As^{+3} and As^{+5} in a coastal sandy aquifer. The study area was located in the Stuarts Point region, northern New South Wales, Australia. A bundled-piezometer was installed in the Holocene barrier of the Stuarts Point coastal sandy aquifer for arsenic species measurement. Vertical distribution was shown two peaks of elevated arsenic concentration along different depth. The first peak was at a depth of 10–11 m,

concentrations of total of arsenic (As^{Tot}), arsenate (As^{+5}) and arsenite (As^{+3}) were in the range of 52–85, 38–67 and 14–18 mg/L respectively and the ratio of As^{+5}/As^{+3} was above 1 at 3.7–2.7. The second peak, at a depth of 25 m, showed the highest concentrations of As^{Tot} , As^{+5} and As^{+3} with values 337, 125 and 212 mg/L, respectively. The As^{+5}/As^{+3} ratio is below 1 at 0.6–0.7. High As^{Tot} and As^{+5} concentrations at shallower depths were related to acidic conditions and very low concentrations of all ions. Desorption of As from Al-hydroxides and As-enriched Fe-oxyhydroxides were probable mechanisms releasing As into the groundwater system. At 25 m, the elevated concentration of As^{Tot} and As^{+3} were potentially associated to the leaching of the clay surfaces. Alkaline pH conditions and high HCO_3^- at this depth presented As^{+3} species in the reducing environment.




V. A. Nguyen, Bang, Viet, and Kim (2009) have investigated contamination of groundwater and risk assessment of arsenic exposure in Ha Nam province, Vietnam. Groundwater samples were collected from private wells 40 samples from four villages in two periods, the dry season on February, 2006 and rainy season in September, 2006. The depths of well ranged from 16–40 m. Human hair samples were used as a biomarker for arsenic accumulation and toxicity in humans, was collected from both male (16) and female (27) at the average age of 26 at least 2 g of human hair samples. Arsenic in groundwater was analyzed by graphite furnace atomic absorption spectrometry (GFAAS, Perkin Elmer 5100) and inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500). The results were found that three out of four studied villages were arsenic contamination. Arsenite (As^{+3}) was predominant species in the groundwater. Sand filtration system was used to treat groundwater for household, but not effective for arsenic removal. Arsenic accumulation in female hair samples was closely related to the arsenic concentration in treating water. In the group of people who used untreated

groundwater has a higher potential carcinogenic rate of 5 in 1,000 people. A higher technology treatment for arsenic removal is essential for minimizing the human health risk.

Hoang, Bang, Kim, Nguyen, and Dang (2010) have investigated the geochemical characteristics of arsenic groundwater. The data were collected from Mekong River delta in Vietnam (MDVN) aquifer during 2007-2008. The soil and water samples were collected from ChoVam village in the Phu Tan District (An Giang Province; CV), and Thanh Binh village in the Thanh Binh district (Dong Thap province; TB). Arsenic in groundwater was analyzed by using inductively-coupled plasma mass spectrometry (ICP-MS; Agilent 7500, USA). The soil samples were analyzed by using the total digestion and the sequential extraction method. In addition, Pearson and Spearman's rho correlations were conducted for analysis and correlation of the parameters. In a study of 460 wells found that 26% of groundwater samples exceeded the WHO guidelines. The elevated arsenic concentration found in the well located within 2 km of the Mekong River bank, which depth less than 60-70 m. The relationship between arsenic and manganese were an inverse. The maximum concentrations of arsenic from An Giang and Dong Thap were found 18 mg/kg and 38 mg/kg at depths of 46 m and 34.5-34.9 m, respectively. Arsenic sediment mainly occurs in the poorly crystalline iron oxide phases. Reductive dissolution of the iron oxide phase is not essential the dominant mechanism of arsenic release to groundwater. Arsenic leaching from sediment to groundwater may control by organic matter, microorganisms, ORP, pH and the combined effects of ions in groundwater.

Bian, Tang, Zhang, Ma, and Zhao (2011) focused on the relationship between arsenic concentrations in the groundwater and geological background in the western Jilin Province, China. Soil samples and groundwater were collected from surface (2–40 cm) and wells at different depths (6 to 160 m). The results was found that in the

horizontal direction, arsenic concentrations that exceeded the standards were distributed in the Huolin River, Tao'er river ended area, the southern part of Taonan city, the central part of Tongyu county, and in the depression between the rivers and low plain in the northern part of the study area. While in the vertical direction, arsenic mainly existed in the phreatic aquifer, which is less than 20 m deep and is enriched in the confined aquifer between 20 and 100 m. GIS was used to demonstrate the correlation between arsenic distribution and the geological background which they are closely related with each other. The tectonic movement, a huge amount of silt and mud slit has an effect on the enrichment arsenic in groundwater in this area.



Chotpantarat, Ong, Sutthirat, and Osathaphan (2011) have investigated the effects of pH conditions on the sorption and transport of heavy metals (Pb^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+}) through the lateritic soil by using column experiment and Hydrus-1D for transportation modeling. The soil samples were collected from Akara mine in Thailand, at a depth between 0 and 2 m below the ground surface. The columns were made from acrylic tubes with 10 cm of length and 2.5 cm of internal diameter. The lateritic soil was packed into the columns by using a wet packing technique. The soil column inflow was 8 mL/hr by using a piston pump. The results were reported by BTCs which the heavy metal was evaluated under two different pH conditions. The transportation of metals was simulated by CXTFIT model and the HYDRUS-1D model was used to evaluate the linear/nonlinear equilibrium and chemical non-equilibrium processes of heavy metal ion sorption and transport in the columns. The experimental showed that Pb^{2+} had the highest sorption capacity and retardation factor at both pH conditions (4.0 and 5.0) and Ni^{2+} had the increasing sorption capacity with increasing pH. The fraction of instantaneous sorption sites (f) of four metal ions on the lateritic soil was persistently about 30%–44% of the whole

sorption sites. The Langmuir isotherm from batch studies with HYDRUS-1D did not predict the BTCs well. However the two-site model (TSM) described the heavy metal BTCs better than the equilibrium linear/nonlinear Langmuir model.

Wongsasuluk, Chotpantararat, Siriwong, Borjan, and Robson (2013) have investigated arsenic contamination in shallow groundwater wells and assessed the impact of human health at Hua Rua Sub-district, Muang District, Ubon Ratchathani province. The twelve samples were collected from wells in agricultural area during June and August 2010 and arsenic was analyzed by using Inductively Coupled Plasma Spectrometry-Mass Spectrometry (ICP-MS). In addition, the questionnaires were used to investigate the behavior of shallow groundwater consume. The results found that the highest concentration of arsenic was 8.98 $\mu\text{g/L}$ on August while the lowest concentration was lower than 0.22 $\mu\text{g/L}$ in June. There are 11 wells were no-acceptable level, which had the Hazard Quotient value of arsenic were higher than one ($\text{HQ} > 1$). In addition, was found that there was only one well, which was a carcinogenic risk (cancer risk $> 10^{-6}$).

Banejad, Mohebzadeh, Ghobadi, and Heydari (2014) have investigated the mathematical model developed for simulation of groundwater flow in the southwest of Hamadan province. Groundwater Modeling Software (GMS) was used to support the MODFLOW-2000 for simulation of flow. After that the model was calibrated in steady state by trial and error and parameter estimation methods by using the data of 1997. The results of modeling showed reasonable agreement between calculated and observed. Finally, MODPATH was used to simulate the advection transport for estimation of flow path and source of contaminants. The results showed that the pollutants moved very slowly from the both sides towards the center of the plain.

