

The dispersivity and retardation factor are required input parameter in contaminant transport models based on the 1-dimensional advection – dispersion equation (Eq. (1)). These parameter describe the hydrodynamic characteristics of soil column. To determine the contaminant transport parameters such as dispersivity (α) or retardation factor (R), we have to design the column experiment for gathering the concentration data of the conservative tracer and the contaminant to determine both of parameters.

For the conservative tracer experiment, we use the conductivity meter (WTW LF 325) to measure the conductivity of sample and convert to concentration of NaCl (mg/L). Then, make the breakthrough curve by plot the relative concentration at pore volume as shown in Figure 4.

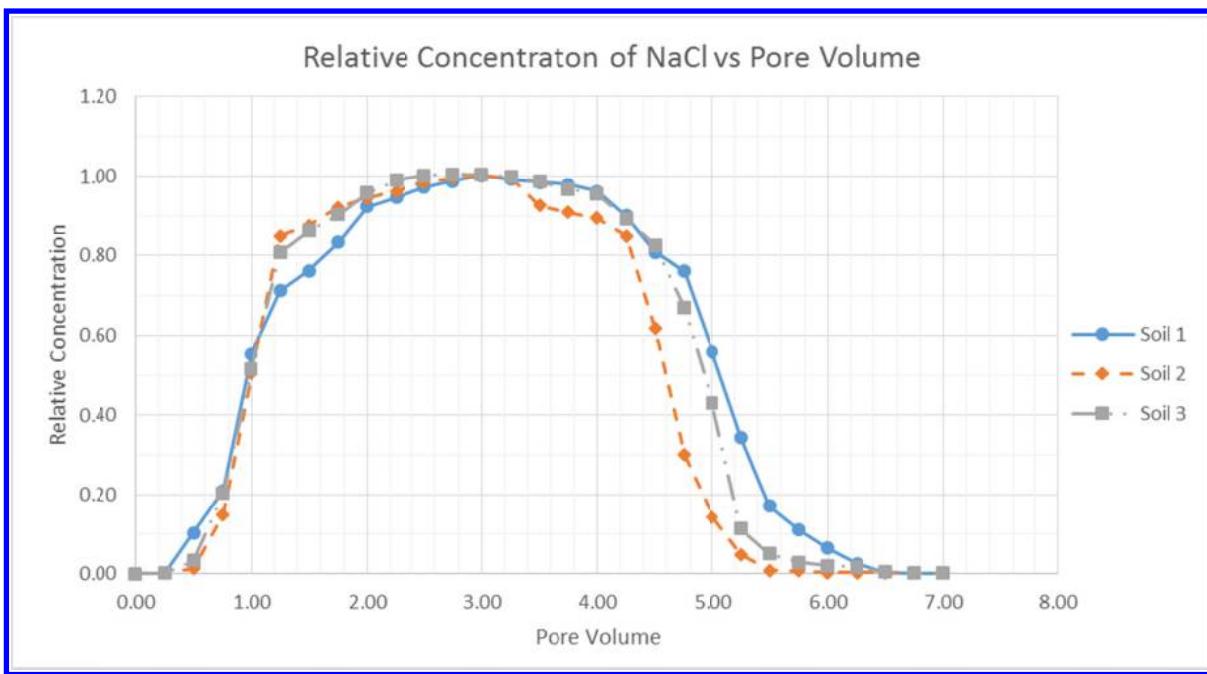


Figure 4 Breakthrough curve of NaCl vs pore volume for soil group 1-3

In Figure 4, the breakthrough curve NaCl are quite similar with other soil groups in the first 3 pore volume which conform to the dispersivity of NaCl as mention in Table 2.

For the contaminant transport, we used the same experimental process with the conservative tracer and analyzed the concentration of 2-Nitrophenol by using Gas Chromatograph (Agilent 7890A). The result of contaminant transport experiment is displayed in the relative concentration of 2-Nitrophenol vs Time as shown in Figure 5.

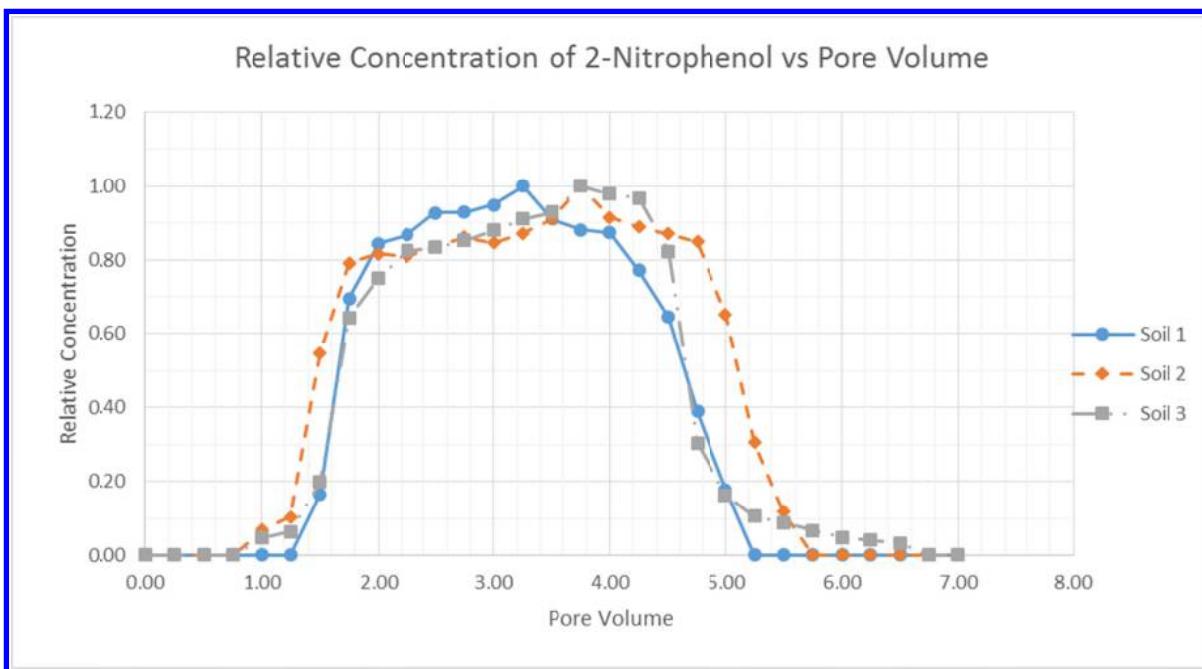


Figure 5 Breakthrough curve of 2-Nitrophenol vs pore volume for Soil Group 1-3

1-dimensional advection dispersion Equation is used to calculate the dispersivity (α) by fitting the dispersivity in Eq (1), (2), (3).

The dispersivity of NaCl and 2-Nitrophenol derived from the transport experiment are provided in Table 2. In case of NaCl, the dispersivity of the column varied from 0.41 – 0.43 cm. Dispersivity for a variety of soils ranges from <0.5 cm. for loamy sand (Perfect et al., 2002). The difference of the dispersivity of NaCl for 3 soil groups is a result of the different pore size and length of soil column that effect to the travel distance in the soil column even use the same flow rate of solution. For contaminant transport experiment, the dispersivity of the column varied from 0.34 – 0.41 cm. The dispersivity of 3 soil columns for 2-Nitrophenol transport experiment are lower than NaCl because NaCl is conservative tracer which has only 2 processes (advection and dispersion) will occur when the solution flow in the column. But in case of 2-Nitrophenol, when the solution pass through the soil column, the chemical reaction or biodegradation are the process which will effect to the 2-Nitrophenol transport characteristic will difference from NaCl. Therefore, the dispersivity of 2-Nitrophenol is less than the dispersivity of NaCl for all 3 soil groups.

Table 2 Dispersivity of NaCl and 2-Nitrophenol for 3 Soil groups

Sample	Dispersivity, α (cm.)	
	NaCl	2-Nitrophenol
Soil Group 1	0.42	0.41
Soil Group 2	0.41	0.34
Soil Group 3	0.43	0.35

The mean residence time (MRT) is the statistical method which used to calculate the average time of solute flow from inlet to outlet of column (Eq. 2). The retardation factor (R) can be calculated by proportion of MRT of solute and MRT of conservative tracer as shown in Eq. (5). The mean residence time of NaCl and 2-Nitrophenol and retardation factor are provided in Table 3. For all 3 Soil groups, the mean residence time of 2-Nitrophenol is more than MRT of NaCl that indicate the 2-Nitrophenol is slower than NaCl.

Table 3 Mean residence time and retardation factor of 3 soil groups

Sample	Mean Residence Time (min)		Retardation Factor (R)
	NaCl	2-Nitrophenol	
Soil Group 1	146.36	164.94	1.127
Soil Group 2	158.45	172.09	1.086
Soil Group 3	155.13	168.51	1.086

CONCLUSIONS

In our study, we got 26 soil samples from our study site and grouping them to 3 groups by using D_{50} of soil sample. For contaminant transport experiment, we selected to use the column experiment for conservative tracer (NaCl) and contaminant (2-Nitrophenol). We determined the contaminant transport parameter by fitting the 1-dimensional advection dispersion equation and calculate the mean residence time of solution. The results of the column experiments described in this study are the 2 contaminant transport parameters: dispersivity (α) and retardation factor (R). The dispersivity of NaCl for 3 soil groups has different value because different pore size and travel distance in soil column. When compare with 2-Nitrophenol, the dispersivity of 2-Nitrophenol less than NaCl due to the chemical reaction and biodegradation process of 2-Nitrophenol fate and transport in soil column. In case of retardation factor which described the transport characteristic of contaminant, the retardation factor of 2-Nitrophenol for 3 soil groups are more than 1 that mean the transport of 2-Nitrophenol is slower than the conservative tracer. Next, the contaminant transport parameter of 2-Nitrophenol will be used to model the contaminant transport in groundwater aquifer and determine the location of potential source of contamination in the study site for the full potential of the source identification problem.

ACKNOWLEDGEMENT

This thesis is supported by Graduate School Thesis Grant, Chulalongkorn University.

REFERENCES

- Bulle, C. S. M., Samson, R., & Deschênes, L. (2011). Transport of chlorinated dioxins and furans in soil columns: Modeling pentachlorophenol pole-treating oil influence. *Chemosphere*, 83(2), 117-123. doi: <http://dx.doi.org/10.1016/j.chemosphere.2011.01.015>
- Guo, M., & Chorover, J. (2003). Transport and Fractionation of Dissolved Organic Matter in Soil Columns. *Soil Science*, 168(2), 108-118.
- Li, G., Xu, Z., Thornton, S. F., & Lerner, D. N. (2000). Transport and degradation of phenol in groundwater at Four Ashes. *Tsinghua Science and Technology*, 5(3), 293-297.

- Li, Z., & Shuman, L. M. (1997). Estimation of retardation factor of dissolved organic carbon in sandy soils using batch experiments. *Geoderma*, 78(3–4), 197-206. doi: [http://dx.doi.org/10.1016/S0016-7061\(97\)00048-7](http://dx.doi.org/10.1016/S0016-7061(97)00048-7)
- Murillo-Torres, R., Durán-Álvarez, J. C., Prado, B., & Jiménez-Cisneros, B. E. (2012). Sorption and mobility of two micropollutants in three agricultural soils: A comparative analysis of their behavior in batch and column experiments. *Geoderma*, 189–190(0), 462-468. doi: <http://dx.doi.org/10.1016/j.geoderma.2012.05.019>
- Perfect, E., Sukop, M. C., & Haszler, G. R. (2002). Prediction of Dispersivity for Undisturbed Soil Columns from Water Retention Parameters. *Soil Science Society of America Journal*, 66(3). doi: 10.2136/sssaj2002.6960
- Pipitsombat, R. (2010). Laboratory-Scaled Investigations and Numerical Modeling of Nitrate Leaching and Transport Characteristics in Saturated Aquifer Systems, Chulalongkorn University: 223.
- Saquing, J. M., Knappe, D. R. U., & Barlaz, M. A. (2012). Fate and transport of phenol in a packed bed reactor containing simulated solid waste. *Waste Management*, 32(2), 327-334. doi: <http://dx.doi.org/10.1016/j.wasman.2011.09.017>
- Sharma, Hari D., and Reddy, Krishna R. "Geoenvironmental engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies."
- Tiedeman, C. R., & Hsieh, P. A. (2004). Evaluation of longitudinal dispersivity estimates from simulated forced- and natural-gradient tracer tests in heterogeneous aquifers. *Water Resources Research*, 40(1), n/a-n/a. doi: 10.1029/2003WR002401
- Todd, D. K. and L. W. Mays (2004). Groundwater Hydrology, Wiley.
- Wilson, J. T., Enfield, C. G., Dunlap, W. J., Cosby, R. L., Foster, D. A., & Baskin, L. B. (1981). Transport and Fate of Selected Organic Pollutants in a Sandy Soil1. *Journal of Environmental Quality*, 10(4). doi: 10.2134/jeq1981.00472425001000040016x

Preliminary Assessment of Groundwater and Surface Water Characteristics in the Upper Chao Phraya River Basin Land Using a Stable Isotope Fingerprinting Technique

Jeerapong Laonamsai¹ and Aksara Putthividhya²

¹Graduate Student, Dept. of Water Resources Engineering, Faculty of Engineering, Chulalongkorn Univ., Bangkok, Thailand 10330. E-mail: teeyoon100@gmail.com

²Assistant Professor, Dept. of Water Resources Engineering, Faculty of Engineering, Chulalongkorn Univ., Bangkok, Thailand 10330 (correspondence author). E-mail: dr.aksara.putthividhya@gmail.com

Abstract

Water stress is rapidly increasing in many parts of Thailand, especially during drought season, due to expansion in agriculture and industry. This study is focusing in the Upper Chao Phraya river basin to assess the capability of using water stable isotope analysis ($\delta D - \delta^8 O$) to refine the understanding on spatial and temporal distribution of precipitation as well as the surface water-groundwater interactions for the aquifer systems underneath the study area. Local precipitation, surface water, and groundwater are sampled along the main river courses and their tributaries. Massive precipitation isotopic composition database from IAEA existing monitoring network (GNIB) along with local Bangkok precipitation isotope signature are compared with precipitation from Chiang Mai province in the North of Thailand to better identify the rainfall isotopic compositions. In addition to the isotopic distinction of precipitation in the area, its impacts on isotopic signature of surface water and groundwater are additionally explored. LMWLs for local rainfall in Bangkok and Chiang Mai are generated with some seasonal variation of rainfall isotope signature due to rain out effect. Surface water in the study area is influenced by evaporation at some degree, revealing that rainfall may not be the primary source of surface water. Yom river's isotope signal values are far more D and ^{18}O -enriched compared to Ping's and Nan's, suggesting the mixing of groundwater into river water and/or the origin of surface water may come from dry-period precipitation. Stable oxygen and hydrogen isotope data in groundwater again fall on an evaporation line, and is thus indicative of the effects of high evaporation rates through the top surficial material. The isotopic similarity with the more depleted δD and $\delta^8 O$ of groundwater samples suggests the potential mixing of groundwater with river water by different mixing processes (54% from river water and 46% from rainfall). The results of stable isotope analyses show correlations in the isotope signature of shallow (i.e., < 50 m deep) and deeper aquifer (i.e., > 50 m deep) which may be associated with hydraulic connection and/or similar hydrogeological conditions. d -excess stable isotope analyses are beneficial to identify the relative contributions of the wet and dry seasonal sources to the groundwater recharge. The results indicate that groundwater sources in the area are composed of an average of approximately 71.4% wet seasonal sources and 28.6% dry seasonal sources.

INTRODUCTION

Environmental isotopes are routinely used in geochemical, hydrological, and hydrogeological investigations. The stable isotopes of oxygen and hydrogen maintain almost the same combination as of the meteoric water, which means it records the status of the initial formed meteoric water, and is a permanent natural tracer (**Clark and Fritz 1997**). Accordingly, after collecting the information of meteoric water and stable isotopes of oxygen and hydrogen in groundwater in a database, and analyzing the hydro-geological structure and the groundwater flow in the target area, one can define the status of mixed groundwater recharge areas and different recharge water sources. Since the combination of stable isotopes of oxygen and hydrogen is constant in normal temperature, the stable isotopes of oxygen and hydrogen can be used as conservative groundwater tracers because values of isotopes remain constant as long as there are no phase changes or fractionation along the flow-path. Moreover, studying stable isotopes of oxygen and hydrogen can help identify different groundwater recharge zones (**Payne and Yurtsever 1974**). In Thailand, stable isotope analyses of water mass were performed in the late 1990s (**Sanford and Buapeng 1996**). These studies provided fingerprints of the hydrologic cycle, such as identification of groundwater age, recharge areas, and seawater intrusion signs. This information becomes very useful for groundwater resources management and numerical modeling (**Sanford and Buapeng 1996; Peng et al. 2002; Kuo and Wang 2001**). The combine study of oxygen and hydrogen isotopes in water sciences has therefore been proven as a promising tool to exploring hydrological fluxes at a regional scale (**Vandenschrick et al. 2002**), including precipitation, groundwater recharge, groundwater-surface water interactions, and basin hydrology (**Gat 1996; Clark and Fritz 1997; Gibson et al. 2005**).

Some area in Thailand has been facing an intensive groundwater exploitation for irrigation purpose during drought season as well as a growing water demand from the extensive industrial development. Our study area is in the upper Chao Phraya river basin located in a large central plain of Thailand where large irrigation serviced fields are scattered all over, leading to an individual private groundwater well installation to compensate the frequent surface water shortage. The uncontrolled heavy pumping has subsequently induced groundwater table decline in some parts of the irrigated areas, causing the severe future groundwater accessibility problems for the entire public water users. This precarious situation definitely asks for the use of the technique of so-called conjunctive water management (**Chun 1964**), in which refers to a management approach similar to Integrated Water Resources Management (IWRM) with the emphasis placed upon the combined use of both surface and subsurface water to meet the total local water demand. Understanding the interactions between groundwater and surface water can be crucial for water resources management, and in the future determination of migration pathways for contaminants. The degree of interactions depends on a number of factors including topography, underlying geology, subsurface hydraulic properties, temporal and spatial variation in precipitation, and local groundwater flow patterns (**Cey et al. 1998**).

Previous research has demonstrated in many areas that groundwater displays a distinctive isotopic signature compared to surface water (**Jacobson et al. 1991; Space et al. 1991; Acheampong and Hess 2000**). The isotopic composition of natural waters can often be used to characterize circulation paths and mixing or exchange processes between surface water and groundwater (**Andreo et al. 2004**). Oxygen and hydrogen isotopes of water are widely used as tracers to understand hydrogeological processes such as precipitation, groundwater recharge, groundwater-surface water interactions, and basin hydrology (**Gat 1996; Vandenschrick et al. 2002; Deshpande et al. 2003; Gibson et al. 2005; Gammons et al. 2006**). A comparison of the oxygen and hydrogen isotopic composition of precipitation and groundwater provides an excellent tool for evaluating the recharge mechanism (**Mizota and Kusakabe 1994; Blasch and Bryson 2007; Heilweil et al. 2009; Yin et al. 2011; Singh et al. 2013**). Determining the surface water-groundwater interactions and sources of groundwater recharge is important for the effective management of groundwater resources. Although considering quite effective, the applications of stable isotope technique in water resources research in Thailand is still extremely rare.

In this study, we aim to investigate the temporal and spatial distribution of rainfall, surface water, and groundwater in the study area of Thailand by employing the stable isotope analysis of ^{18}O and ^2H . Since IAEA has collected and analyzed worldwide isotopic compositions of water since 1961 from the existing monitoring network (GNIB), stable isotopic signature of rainfall from Bangkok (Capital city of Thailand) is compared with precipitation from Chiang Mai province to better identify the isotopic compositions of rainfall. Moreover, rainfall from the Northern Thailand is collected and analyzed for its isotopic composition. In addition to the isotopic distinction of precipitation in the area, its impacts on the isotopic signature of surface and groundwater along the major river and irrigation canal in the upper Chao Phraya basin is also investigated. This study is claimed as one of the pioneer work in applying the isotopic fingerprinting technique to preliminarily assess the hydrologic characteristics in upper Chao-Phraya river basin of Thailand. The results from this work provide useful information about hydrological processes such as the interactions of precipitation and surface water as well as groundwater entity in the study area.

MATERIALS AND METHODS

STUDY AREA

The upper Chao Phraya plain of Thailand shown in Fig. 1 covers about 38,000 km^2 (approximately 180 km × 300 km) in 8 provinces with a population of 4 million people. The main landuse is 63% agriculture, out of which 21% is irrigated, and 24% is devoted for forestry. More than 90,000 groundwater wells exist in the region to serve as primary and secondary source of water supply.

Ping, Wang, Yom, and Nan Rivers are abundant in runoff and also high in sediment transport capacity. Most surface water is utilized for agricultural purposes in rainy season. Domestic and industrial water rely on water supply and groundwater. Agricultural sector also use groundwater in conjunction with surface water in dry

period. To understand the use of water resources in this basin, the fundamental characteristics and recharge sources of the groundwater aquifer need to be analyzed.

The main groundwater basin is divided by 5 major rivers that flow from North to South and formed the geological basis as a depositional flood plain. The basin is surrounded in the East and West by mountains of volcanic rocks. The average elevation of the basin is 40-60 m above MSL. The basin drains into the lower basin in the South, though the free discharge is partially obstructed by crystalline rocks. Annual rainfall of 900-1,450 mm in the study region is appointed to 81% in the wet (April-September) and 19% in the dry season (October-March). Plychumpol irrigation project is also located in upper Chao Phraya plain and covers about 140 km² (20 km × 70 km) of both Pitsanulok and Pichit provinces with a population of 16,000 households. Main surface water basin is dissected by Yom and Nan rivers, which drain from North to South. Irrigation water is diverted from Nan River at Naresuan diversion dam. The groundwater aquifer forms the geological basis as a depositional flood plain from North to Southeast with mountains of volcanic rocks surrounded in the West. More than 3,000 groundwater wells exist in this area and there are several groups of intensive groundwater extraction. The groundwater aquifers were defined using the concept of the hydrostratigraphic units which are geological conditions of similar hydrogeologic properties and their confining boundaries. The aquifer system in this study was defined as two-layered aquifer, whereby the thickness of the upper, semi-confining layer varied between 10-70 m and lower confining layer between 100-300 m.

STABLE ISOTOPE SAMPLE COLLECTIONS

Precipitation, river water, and groundwater samples were collected for oxygen and hydrogen isotopic analyses from 2007-2008. Sampling was carried out during both wet and dry periods. Sampling procedures for precipitation were in accordance with IAEA guidelines (International Atomic Energy Agency 1983). The procedures are designed to avoid evaporation of precipitation samples. Sampling locations are shown in Fig. 2. Surface water and groundwater were sampled from 44 locations distributed throughout the study area. Each sample was collected using the following sampling bottles: 2×1-L glass bottles, 250-mL plastic container, and 2×60-mL glass bottles cooled with ice and stored in a dry place immediately after sampling. The 37 groundwater samples were collected at the depth between 15 to 120 m below ground surface. Taking the hydrologic conditions of the study area into account, the groundwater samples were classified into shallow groundwater (0-50 m below ground surface) and deep groundwater (more than 50 m below ground surface). Seven surface water samples, composed of water from streams and irrigation canals, were collected along the flow path of surface water in the irrigation project.

Stable oxygen isotopic compositions were analyzed using the CO₂-H₂O equilibration method (**Epstein and Mayeda 1953**). The equilibrated CO₂ was measured using a VG SIRA 10 isotope ratio mass spectrometer. The hydrogen isotopic compositions were determined on a VG MM602D isotopic ratio mass spectrophotometer after was reduced to H₂ using zinc shots made by the Biogeochemical Laboratory of Indiana University (**Coleman et al. 1982**). All isotopic

ratio resulted were reported as the δ -notation (‰) relative to the international VSMOW (Vienna Standard Mean Ocean Water) standard.

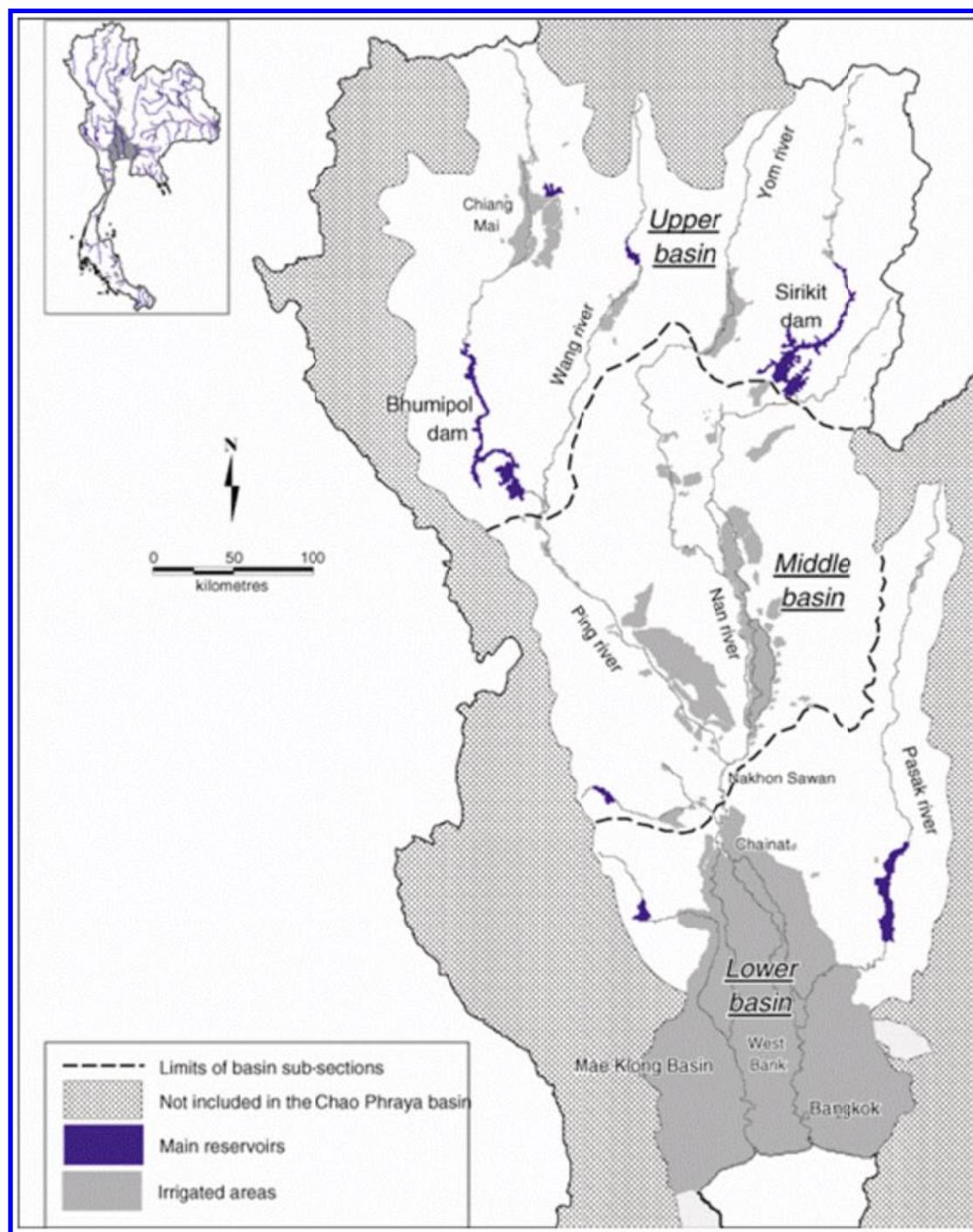


Fig. 1. Study Area (Upper Chao Phraya River Basin)

Physico-chemical parameters, electrical conductivity (EC), pH, total dissolved solids (TDS) and temperature were also measured at each sampling point. Major ion concentrations were analyzed using Ion Chromatography at the Department of Groundwater Resources, Thailand.

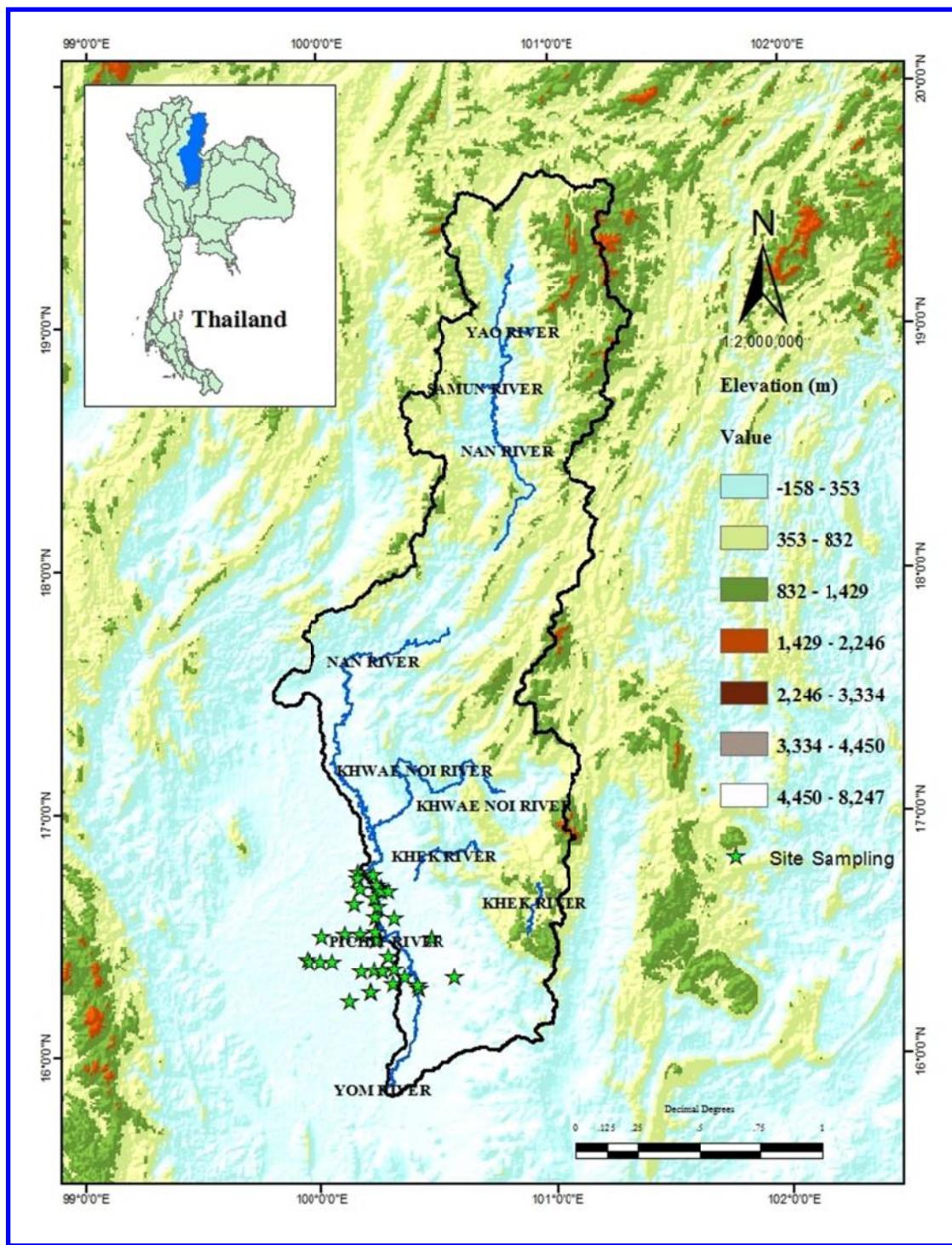


Fig. 2. Sampling Sites