ENVIRONMENTAL IMPACT OF IRRIGATION TO GROUNDWATER CONTAMINATION AND AQUIFER VULNERABILITY FROM INTENSIVE AGRICULTURAL PRACTICES IN THAILAND

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ABSTRACT

Irrigation has contributed significantly to poverty alleviation, food security, and improving the quality of life for rural populations. However, infiltration of irrigation water in excess of available root zone storage from agricultural lands with poorer water quality may carry both agricultural chemicals and naturally recharge to groundwater, rivers, and lakes. In recent years water security concerns have centered on groundwater depletion by withdrawals for irrigated agriculture and groundwater quality degradation both from natural and anthropogenic origin, and only limited attention has been paid to the more insidious (and more chronic) problems of progressive aquifer contamination of groundwater recharge by irrigation return flows, which is occurring in major intensive agricultural practices. Environmental vulnerability and risk assessment is a step towards identification, analysis, and classification of vulnerable and risk factors as well as its long-term implications, and thus reduction of the possibility of adverse consequences from irrigation, are the primary objective of this present study. A novel approach for environmental impact of irrigation to groundwater contamination and aquifer vulnerability assessment is initiated and applied by combining a novel aquifer vulnerability DRASTIC map with pollution severity and prioritization based in probability of occurrence of pollution using TOPSIS ranking method. 9% of the total study area is categorized as high risk level which needs intensive groundwater samples from domestic and monitoring wells at various depths (100 samples from <30 m deep, and 60 samples from >60 m deep) are collected and analyzed for nitrate (as NO_3^-), K. sulphate (as SO_4^{2-}) and other water quality parameters. NO_3^- level in groundwater ranged from 0.18 to 151 mg/L. Consistent K and NO_3^- trends from municipal wells in the study area indicate that nitrate source is likely agricultural origin. Detection of high nitrate concentration in shallow groundwater suggests the direct association of major nitrate concentration in groundwater aquifer with potential surficial source on the ground.

Keywords: Groundwater contamination, irrigation, nitrate, agricultural contamination, contaminant transport and migration, MODFLOW, MT3D

1. INTRODUCTION

Groundwater represents about 30% of world's freshwater, from the other 70% captured in the ice caps (69%) and rivers and lakes (1%). Groundwater counts in average for one third of freshwater consumed by humans and can be as high as 100% in some parts of the world. Kingdom of Thailand, a country with a population of over 65 million people and a catchment area of 513,120 km^2 with average annual rainfall of 1,430 mm and the estimated total annual water resources of 215,000 Mm^3, is currently abstracting groundwater more than 11,047 Mm^3 for agriculture (4,840 Mm^3 or 44%), industry (4,085 Mm^3 or 37%), and domestic use (2,122 Mm^3 or 19%) in dry season and mainly employed in rural areas (Department of Groundwater Resources Thailand, DGR 2019). Long-term population growth and economic development is placing ever-increasing demands on water resources. The stress on water in the main development regions is more profound, and groundwater has become an imperative resource for industrial use and urban water-supply. A consequence of recent droughts has additionally simulated more extensive groundwater exploitation for dry-season cropping (rice, in particular) in both irrigated and rain-fed agricultural land. It has been estimated that while only 40,000 million m^3 of surface water (saved in rivers, lakes, and dams) is accessible annually, as much as 1.1×10^6 million m^3 of groundwater stored underneath Thailand's subsurface aquifer systems is available with average annual recharge of 10^5 million m^3. Recent floods, droughts, water pollution, and increase in water demand clearly emphasize the need for an integrated development of water resources (i.e., both surface water and groundwater) and effectively implemented water management schemes (structural, non-structural, institutional, economics, finances, etc.) in Thailand to ensure water security, sustainability, and efficiency of its valuable groundwater resources for greater societal benefits.

Intensive agricultural practices in Thailand nowadays present a direct threat to the country's clean groundwater supply. Agricultural practices eventually lead to non-point sources of groundwater pollution, and their effects accumulate over time (**Liu et al. 2005**). In the last 40 years, there has been more than 700% increase in global fertilizer consumption, and it is one of the main driving factors of water quality degradation (**Foley et al. 2005; Scanlon et al. 2007**). Nitrogen (N) is one of the common essential inputs to ensure sustainability of agriculture (**Schröder et al. 2004**), and Nitrogen loss from farmland also continuously accumulates in groundwater and pollutes the artesian wells that people end up using for drinking water. Nitrate is one of the most widespread agricultural contaminants found in aquifers around the world and is present mainly in human and animal wastes (**Batlle Aguilar et al. 2007**).

Nitrate is well known for its highly water-soluble characteristics and can be easily transported through unsaturated soil to groundwater due to its negative charge. Aqueous nitrate has no taste and odor-less and can be detected through a chemical analysis only. Natural-origin nitrate is generally associated with less than 2 mg/L nitrate N concentration. Strong correlation and connection between agriculture and nitrate concentration in groundwater have been studies and reported (**Liu et al. 2005; Putthividhya and Pipitsombat 2015**). Drinking water with high levels of nitrate can cause various health problems, especially a temporary blood disorder known as "methemoglobinemia" or "blue baby syndrome" (**Camargo and Alonso 2006**) in infants or children younger than 6 months old (**World Health Organization 2006**). Some studies (**CDPH 2013; Wolfe and Patz 2002**) reported that risk factors for several types of cancers including gastric, colorectal, bladder, urothelial and brain tumor are engaged with long-term exposure to high nitrate levels in drinking water. As such, controlling and monitoring nitrate transport, tracing for nitrate sources, as well as modeling potential risks of future nitrate migration extent in subsurface aquifer systems around intense agricultural farmlands are critical for planning and controlling anthropogenic nitrate occurrence in sustainable groundwater resource management.

In Thailand, soil and groundwater pollution has continued to increase due to population growth and agricultural development in the past decades and fertilizer consumption has continued rising since 2004 and reached its maximum of 167.1 kg/hectare of arable land in 2013. **Asanachinda (1996)** discovered high nitrate concentrations up to 290 mg/L in groundwater samples collected from agricultural areas in Chiang Mai, which is considered one of the pioneer discoveries of nitrate accumulation in surface water and shallow groundwater in Thailand. Later on, aqueous nitrate in groundwater suspected to be fertilizer-origin had been encountered in Suphanburi and Kanchanaburi from 6 (out of 21) groundwater samples with maximum concentration level (MCL) greater than 50 mg/L (**WHO** drinking water standard for nitrate; **Tirado 2007**). **Putthividhya and Pipitsombat (2015)** collected more than 100 groundwater and soil samples from Suphanburi province in 2014, analyzed for nitrate concentrations in environmental samples, and groundwater contamination spatial map was generated. Regional assessment of groundwater contamination from agricultural source initiated since 2014 (**Putthividhya and Pipitsombat 2015**) not only provided the string evidence of nitrate contamination in soil and groundwater, but also located the nitrate hotspots that can benefit for soil and/or groundwater pollution control, prevention, and monitoring programs.

From the initial long-term monitoring on the current status of nitrate contamination and migration in groundwater from agricultural practices in Thailand, we aim to follow-up on investigating the nitrate levels in groundwater in Suphanburi due to the continuous intensive agricultural activities with excess fertilization. Collection and analysis of more than 160 groundwater samples from domestic and monitoring wells at various depths (100 samples from <30 m deep, and 60 samples from >30 m deep) were undertaken for nitrate (as NO3-) , K, sulphate (as SO_4^{2-}) and other chemical parameters in this study. Six column experiments were conducted using 3 representative porous media groups/sub-classes under low and high flow conditions to explore the transport characteristics of aqueous nitrate. The numerical model was developed to generate regional groundwater flow characteristics and piezometric level distributions using the USGS 3D finite-difference code MODFLOW-2000. The well calibrated regional groundwater flow model was coupled with MT3D model to simulate laboratory- and regional-scaled aqueous nitrate transport as well as to project farfuture nitrate migration characteristics using estimated and measured hydrogeological field parameters. Future applications of the model can be used to test "what-if" scenarios to improve effectiveness and efficiency of potential nitrate management, planning, and monitoring programs.

2. MATERIALS AND METHODS

2.1 Study area

Suphanburi is about 100 km west of Bangkok. Approximately 35% of this area is paddy fields and farmland with rice and sugarcane as major crops. Averaged annual rainfall of 976 mm (data from Year 1989-2017) is reported for the entire province with the peak rainfall in September. **Ramnarong (1993, 1998)** described that the study area is hydrologically divided into highlands on the West and lowlands in the Eastern and Southeastern regions. Floodplain deposit is the main hydrogeological characteristic of the study area, while the western areas are consolidated aquifers composed of granite and volcanic rocks. This unconsolidated formation provided low quantity and quality of groundwater with field estimated yield of 12-50 m^3/hr. The main groundwater source for consumption and agricultural use was extracted from the upper shallow aquifer which was less than 50 m deep.

Kanchanaburi province is located further in the west of Thailand approximately 250 km from Bangkok. Its elevation ranges from 140 to 1046 m MSL with an averaged slope of 66%. Geology mainly composes of terrain and colluviums deposit of Quaternary and Ordovician limestone. Annual rainfall ranges from 1250 to 1940 mm with an average of 1663 mm. An average number of rainy days is 137 days of which 83 days (60%) and 42 days (30.7%) are recorded with rainfall less than 10 mm and 10-30 mm, respectively. The wet period starts from April to October and the rest of the year is considered dry. **Table 1** presents monthly average precipitation records in Suphanburi and Kanchanaburi from 1981-2020.

Table 1. Average monthly precipitation of Suphanburi and Kanchanaburi province (from year 1981-2019; Source: Thai Meteorological Department).

Month	Jan	Feb	Mar	Apr	May	June
Suphanburi Rainfall (mm)	3.7	6.9	18.9	49.1	114.3	94.4
Kanchanaburi Rainfall (mm)	3.3	18.2	29.0	78.5	145.3	86.4

Month	July	Aug	Sep	Oct	Nov	Dec
Suphanburi Rainfall (mm)	98.8	118.4	223.4	196.7	44.1	6.7
Kanchanaburi Rainfall (mm)	102.9	98.3	220.5	209.2	58.6	6.2

2.2 Groundwater sampling and analyses

Total of 160 groundwater samples from domestic and monitoring wells at various locations (**Figure 1**) and depths (100 samples from <30 m deep, and 60 samples from >30 m deep) were collected based on the previous groundwater quality analyses (**Putthividhya and Pipitsombat 2015**). Samples were carefully preserved and transported back for further chemical parameter analysis at a certified analytical laboratory in Bangkok. The environmental parameters include: total hardness as $CaCO_3$, non-carbonated hardness as $CaCO_3$, TDS, BOD, alkalinity, Fe, Mn, Cu, Zn, SO_4, Cl, F, nitrate (NO_3^-), As, CN^-, Pb, Hg, Cd, Se, Hexavalent Cr, and Ni. Soil texture, primary land use, well depth, annual averaged rainfall, groundwater recharge, and spatial concentration distribution of nitrate were processed in the ArcGIS environment.

2.3 Laboratory-scaled nitrate transport column experimental setup

Grain size distribution (GSD) of the representative soil samples were generated from sieve analysis of the 10 representative soil samples systematically collected from the study area. Sieve analysis revealed that most soil samples were fine to medium fine with average particle sizes of 0.4-0.7 mm. Three individual soil classifications (S2, S3, and S8) based on KMEANS clustering of all the measured grain size distributions previously analyzed (**Putthividhya and Pipitsombat 2015**) were employed in a series of laboratory-scaled column experiments to investigate nitrate transport characteristics. The physical characteristics of representative soil samples could be classified based on ASTM Standard Practice for Classification of Soils for Engineering Purposes (**ASTM Standard D2487**). Soil samples S2 (d_{50} = 1.3 mm) and S8 (d_{50} = 0.7 mm) were classified as ***SW*** described as clean sands (more than half of coarse fraction was smaller than No.4 sieve size with wide range in grains sizes and substantial amount of all intermediate particle sizes). While soil sample S3 (d_{50} = 2.5 mm) was classified as ***SP*** described as clean sands (more than half coarse fraction was smaller than No.4 sieve size with predominantly one size or a range of sizes with some intermediate sizes missing).

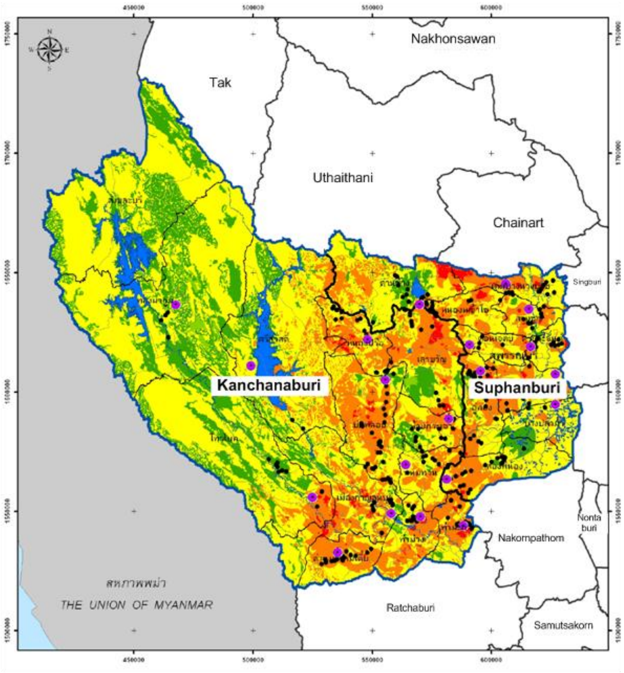

Figure 1. Study area with groundwater sampling points.

The column experimental setup is demonstrated in **Figure 2**. 520 ppm NaCl solution was employed as a conservative tracer in all experiments. Chloride ions were analyzed on a Microprocessor Conductivity Meter. A cylindrical borosilicate glass column (inner diameter 2.5 cm, length 10 cm, Kontes) was used as a container for porous media. The prepared soil sample was wet packed into the clean column following the procedures previously described by **Putthividhya (2004)**. After packing, the packed column was flushed with Milli-Q water overnight for at least 10 pore volumes (PVs) at the designated flow rate, followed by 5 PVs of 520 ppm NaCl solution. Then, the column was flushed with 400 ppm nitrate solution through the column inlet for 5 PVs. Steady state effluents from the column were constantly collected using a fraction collector at the outlet.

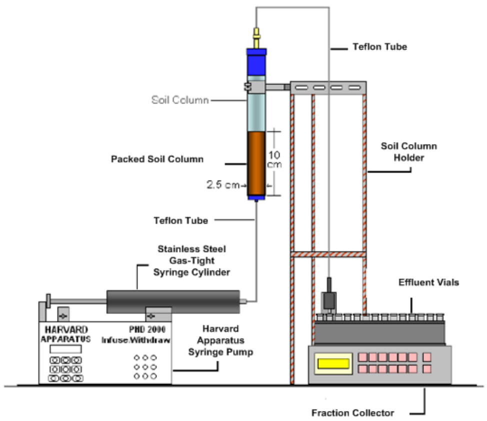

Figure 2. Laboratory-scaled nitrate transport and leaching experimental setup.

2.4 Numerical modeling of groundwater flow and nitrate transport characteristics

The simulation task was generally composed of 2 main components: the simulation of groundwater movement/flow and the simulation of solute transport. MODFLOW groundwater model was employed to deal with the hydrodynamics of the steady-state 3D groundwater flow through porous media. MODFLOW is a fully distributed model that calculates groundwater head and flow from aquifer characteristics. It generally solves 3D groundwater flow equation using finite difference procedure requires that the aquifer be divided into cells (grid cells), whereas the aquifer (hydraulic and hydrogeological) properties are assumed to be uniform. The following basic equation is solved by MODFLOW (**Bazagan-Lari et al. 2009**).

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)-w=S_s\frac{\partial h}{\partial t} \quad (1)$$

where K_{xx}, K_{yy}, and K_{zz} = hydraulic conductivities along the X, Y, and Z directions, respectively

w	=	source or sink of water
h	=	groundwater head
$\boldsymbol{S_s}$	=	specific storage of aquifer materials
t	=	time

A finite-difference grid consisted of 135 rows, 77 columns, and 2 layers (based on the real aquifer geological structure). Grid sizes were varied from 250×250 m (in general) to 50×50 m near the sampling wells and piezometers. The simulation period was taken from 1 January 2013 to 28 February 2017 with daily time steps. The basic input data set to the flow model were piezometric levels and discharge by wells as well as aquifer parameters, including topography, geometry, and soil properties. The unknown head in each cell is calculated at a point or node at the center of the cell (**Conan et al. 2003**). It was able to predict future changes of groundwater potentials and change in flow direction.

Solute transport in groundwater system was simulated using a 3D solute transport model MT3D which can simulate advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems. Governing partial differential equation describing the fate and transport of any contaminants for species ***k*** in 3D, transient groundwater flow systems can be formulated as shown in **Equation 2** (**Zheng 1990**).

$$\frac{\partial(nC^k)}{\partial t} = \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial C^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(nV_{ij}C^k\right) + q_s C_s^k + \sum R_n \qquad (2)$$

where	$\boldsymbol{C_k}$	is	the dissolved concentration of species ***k***
	w	is	the porosity of the subsurface medium
	t	is	the time
	$\boldsymbol{x_i}$	is	the distance along the respective coordinate axis
	$\boldsymbol{D_{ij}}$	is	the hydrodynamic dispersion coefficient tensor
	$\boldsymbol{V_{si}}$	is	the seepage or linear pore water velocity $= \frac{q}{n}$
	$\boldsymbol{q_s}$	is	the volumetric flow rate per unit volume of aquifer representing fluid sources (+) and sinks (-)
	$\boldsymbol{C_{sk}}$	is	the concentration of the source or sink flux for species k
	$\sum R_n$	is	the chemical reaction

The steady state case in MODFLOW was adopted to simulate the regional groundwater flow patterns in the study area. Hydraulic properties of the stratigraphic units were taken from Department of Groundwater Resources, Thailand. The true longitudinal hydraulic conductivity was initially assumed to be 10 m/d for the silt-clay cap and ranged among 50 and 100 m/d for the sand-gravel stratigraphic units. The transverse hydraulic conductivity was assumed for only 10% of the longitudinal value. The initial heads and boundary conditions were extracted from 1:100,000 hydrogeological maps of the Western region of Thailand, consisting of a combination of impermeable and constant-head cells representing rivers, hills, and valleys in the study area. The effective porosity and transmissivity were assumed as constant average values of 0.25 and 14.51-50.30 m^2/d, respectively. The calculated steady-state groundwater levels and the direction of regional groundwater flow were calibrated and verifies with the observed dataset. Modeling outputs included determining the continuous groundwater levels in the study area and the values of solute concentrations and distribution in the region at different time steps.

3. RESULTS AND DISCUSSION

3.1 Nitrate in groundwater

The distribution of nitrate in groundwater in Suphanburi province was previously assessed in 2000 and 2014 (**Putthividhya and Pipitsombat 2015**). The results indicated that abundant of soluble nitrate has been detected in the aquifer systems since 2000 as tabulated in **Table 2**. U-Thong (central part of Suphanburi) and Song-Pee-Nong (southern part of Suphanburi) were subjected to the most severe contamination. In this work, groundwater samples were taken to evaluate the extent of nitrate contamination in Suphanburi (from the same municipal wells and monitoring wells previously sampled). The current spatial nitrate distribution in groundwater was compared with the results previously examined and shown in **Figure 3**.

Since naturally occurring nitrate concentrations are generally less than 2 mg/L nitrate N, nitrate concentration detected in the environmnet greater than 2 mg/L should be considered anthropogenic-origin. Using the nitrate MCL of 45 mg/L, the results in **Figure 3** indicated that the extent of nitrate contamination in groundwater was expanding within 3 years time span (from year 2014 to 2017). Some nitrate hotspots, particularly in Song-Pee-Nong (southern part of Suphanburi), Nong-Ya-Sai (northern part of Suphanburi), and Dan-Chang (northwestern of Suphanburi), were diminished and nitrate concentration detected in groundwater was relatively lower than 45 mg/L. However, the majority of nitrate former hot spots still noticeably existed with nitrate concentrations up to 100 mg/L, i.e., in Derm-Bang-Nang-Buad and U-Thong. To make the story worse, the new nitrate hot spots with fairly high concentrations up to 158 mg/L were discovered based on the investigation in this work near Muang and Southern Song-Pee-Nong districts shown in **Figure 3**.

Table 2. Comparison of maximum soluble nitrate concentrations in groundwater in Suphanburi from long-term monitoring (year 2000-2017).

Location (District)	Maximum Soluble Nitrate Concentration in Groundwater (mg/L)		
Suphanburi Province	Sampling Year		
Thailand	2000	2014	2017
U-Thong	47 mg/L (Well No. MT48, 37 m Deep)	91 mg/L	85 mg/L
Derm-Bang-Nang-Buad	130 mg/L (Well No. MN164, 37 m Deep)	97 mg/L	57 mg/L
Song-Pee-Nong	110 mg/L (Well No. MN99, 11 m Deep)	77 mg/L	69 mg/L
Muang	54 mg/L (Well No. MN237, No Information on Well Depth)	99 mg/L	74 mg/L
Dan-Chang	< 45 mg/L	72 mg/L	< 45 mg/L
Bang-Pla-Ma	< 45 mg/L	70 mg/L	< 45 mg/L
Don-Je-Di	< 45 mg/L	< 45 mg/L	< 45 mg/L
See-Pra-Chan	< 45 mg/L	< 45 mg/L	< 45 mg/L
Nong-Ya-Sai	< 45 mg/L	< 45 mg/L	95 mg/L
Sam-Chuk	< 45 mg/L	< 45 mg/L	< 45 mg/L

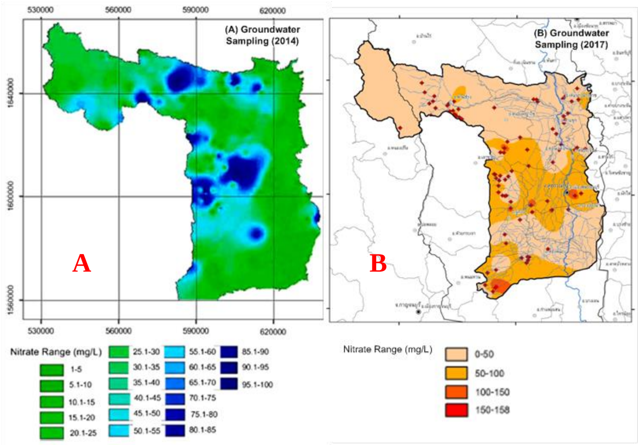

Figure 3. Extent of the spatial soluble nitrate contamination in groundwater in Suphanburi province: (A) data from groundwater sampling in 2014; and (b) data from recent groundwater sampling in 2020.

Variation of nitrate concentrations in groundwater as a function of sampling depths is also presenting in **Figure 4**. Groundwater samples were taken from municipal and monitoring wells in the study area, which could be divided into 2 groups based on well's depths, i.e., a) well depth < 30 m; and b) well depth > 30 m. 100 groundwater samples were collected from a series of wells with < 30 m deep and analyzed for soluble nitrate concentrations as well as other chemical parameters. The results indicated that our shallow groundwater was contaminated with nitrate at concentrations ranged between 0.50-150 mg/L with an average value of 30 mg/L. We have also discovered that 30 groundwater samples (out of 100 samples) collected from sampling wells with less than 30 m deep (i.e., 30%) were contaminated with aqueous nitrate concentration exceeding MCL of 45 mg/L. Next, 60 groundwater samples were compiled from a series of wells with > 30 m deep and analyzed for nitrate concentrations as well as other chemical parameters. The deeper groundwater was contaminated with nitrate at concentrations ranged between 0.10-100 mg/L with an average value of 25 mg/L. We have also discovered that 14 groundwater samples (out of 60 samples) collected from sampling wells deeper than 30 m were contaminated with aqueous nitrate concentration exceeding MCL of 45 mg/L. Moreover, the maximum nitrate concentration of 150 mg/L were detected in groundwater at approximately 15 m deep below ground surface, while the water table was typically detected at 5-20 m below ground. The results revealed that 30% of shallow groundwater (< 30 m deep) and 23% of deeper groundwater (> 30 m deep) were contaminated with nitrate, suggesting the direct association of major nitrate contamination in groundwater with potential sources above ground.

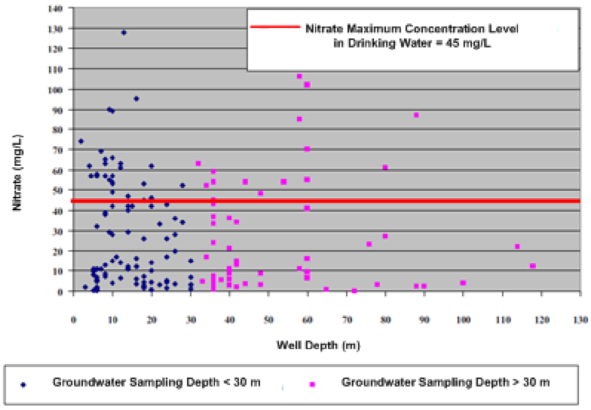

Figure 4. Variation of Nitrate in groundwater from Suphanburi and Kanchanaburi as a function of sampling depths.

3.2 Nitrate in soil vs. crop types

Due to abundant surface water and groundwater supply in the study area, farmers prefer to grow a variety of crops, e.g., maize, rice, vegetables, potatoes, orchards, sugarcanes, etc. Soil samples from various agricultural farmlands were collected and analyzed for leftover nitrate concentrations. The results illustrated in **Figure 5** indicated that soil samples were heavily contaminated with nitrate from land directly associated with vegetable farming. The regional-scaled land use map (**Agrimap 2017; Land Development Department 2016**) suggested that the majority of land in the study area was occupied by rice paddy fields. Interestingly, our analysis showed that rice paddy fields generated relatively less excess nitrate in soil compared to vegetable farming. This finding was fairly consistent with the previous report of maximum nitrate concentration level (MCL) in groundwater collected from Asparagus farms (**Tirado 2007**). Sugarcane, on the other hand, was the second most popular agricultural products growth in the study area with the second highest leftover nitrate concentration discovered in both soil and groundwater. More detailed studies on N fertilization patterns on agricultural yield and leftover -N and nitrate should be conducted for optimized fertilization in intensive agricultural region in Thailand.

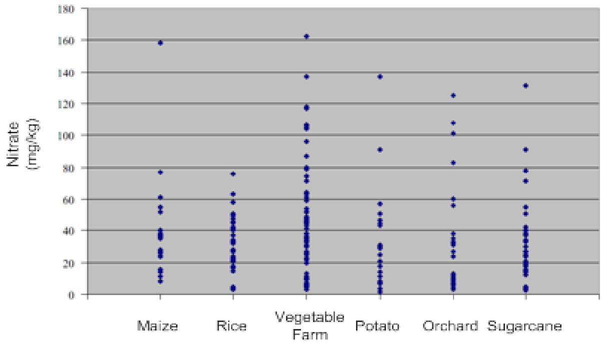

Figure 5. Variation of nitrate in soil samples collected from various agricultural practices in the study area.

3.3 Laboratory-scaled column transport experiments and model simulation

Three soil sub-classes (namely S2, S3, and S8) were employed in a series of laboratory-scaled column experiments to investigate nitrate transport characteristics under low and high flow conditions. Aqueous nitrate solution was constantly fed into the packed bed column via the influent line. Steady-state effluents from each column were carefully collected using a fraction collector. **Figure 6** presents steady-state normalized breakthrough curves (BTCs) plotted as a function of time demonstrating aqueous nitrate transport characteristics in soils S2, S3, and S8 under saturated low (40 mL/hr) and high (60 mL/hr) flow conditions. Nitrate BTCs in all tested soil did not quite reach steady state, unlike conservative tracer's (i.e., chloride). After switching the influent line from nitrate solution to Milli-Q water, nitrate concentration decreased and the slope of the normalized concentration curve for nitrate was relatively flatter, resulting in observed longer tailing effects at the late time of the experiments. The observations also indicated a slower nitrate removal out of the column compared to chloride, especially when the system was operated at lower flow rate.

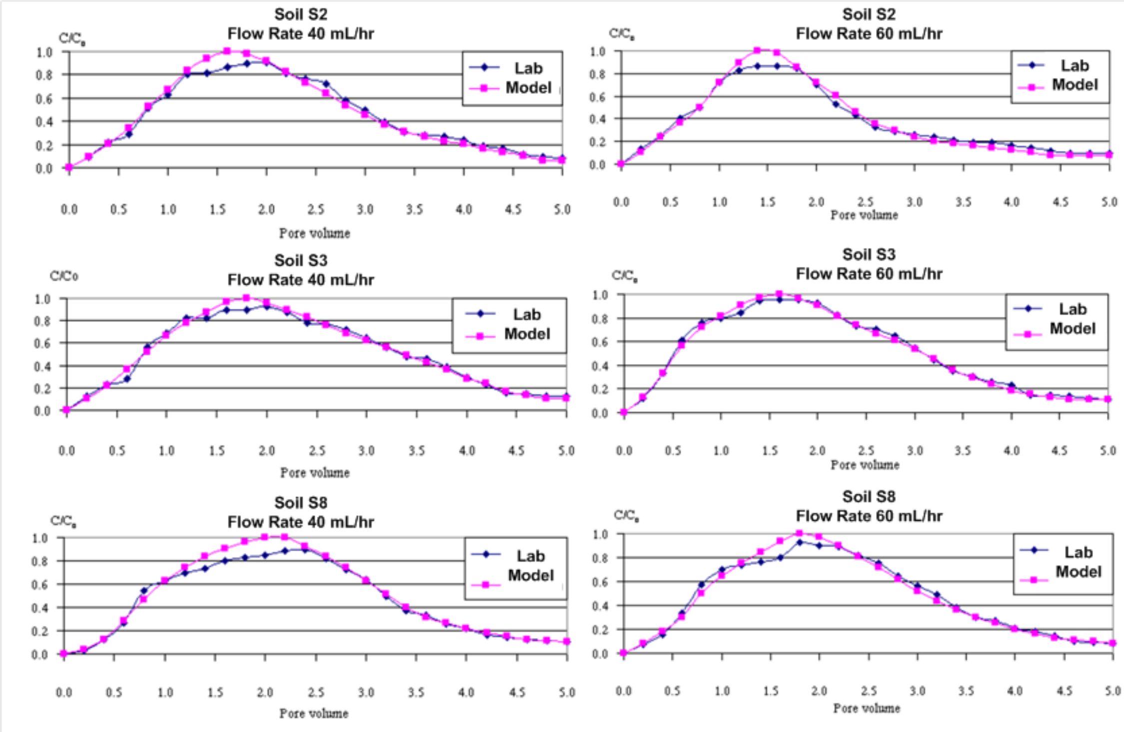

Figure 6. Experimental and model simulation of steady-state normalized breakthrough curves (BTCs) of nitrate transport characteristics in soil S2, S3, and S8 under saturated low (40 mL/hr) and high (60 mL/hr) flow conditions.

The mean residence time of each column experiment could also be calculated from the BTCs as tabulated in **Table 3**. At identical flow rate conditions, soil S3 resulted in the lowest mean hydraulic retention time, suggesting the shortest time solute particles were in contact with the porous media. Water could travel faster with increasing flow rate, resulting in lower hydraulic retention time by 31.8%, 37.7%, and 37.1% for soil S2, S3, and S8, respectively. When comparing nitrate transport characteristics among the 3 sub-classes of representative soils collected from the study site, nitrate seemed to arrive later than the conservative tracer in 2 out of 3 soils tested. For S3 soil sample (the coarsest one), an early breakthrough of nitrate was observed, suggesting that a significant pore exclusion occurred. Nitrate retardation factors for all 3 soil columns operating under low and high flow rates were calculated and presented in **Table 3**. The retardation factors ranged from 1.05 to 1.25 (depending on soil types and flow rates). Reduction in retardation factors was considered insignificant with increasing flow rate due to an equilibrium mass transfer conditions at both low and high flow rate operation. Existing less pronounced tailing effects in the case of higher flow rate conditions also supported the equilibrium behavior among aqueous and sorbed phases.

Table 3. Summary of flow characteristics mean residence time, retardation factors, and dispersivities from nitrate transport column experiments and model simulation.

Properties	**Flow 40 mL/hr**			**Flow 60 mL/hr**		
	S2	**S3**	**S8**	**S2**	**S3**	**S8**
Porosity, -	0.42	0.41	0.41	0.42	0.41	0.41
d_{50}, mm	1.3	2.5	0.7	1.3	2.5	0.7
Mean Residence Time, min	63.98	54.50	66.82	43.65	33.93	42.03
Retardation Factor, ***R***	1.08	1.11	1.05	1.07	1.10	1.05
Longitudinal Dispersivities (α), cm (from Column Experiment)	2.41	4.53	2.32	2.79	4.94	2.57
Longitudinal Dispersivities (α), cm (from Model MODFLOW and MT3D)	2.35	3.10	2.20	2.65	4.90	2.57

Table 4. Summary of hydrodynamic input parameters for MT3D nitrate transport simulation.

Soil Sample	Flow Rate					
	40 mL/hr			60 mL/hr		
	S2	S3	S8	S2	S3	S8
Initial Nitrate Concentration, mg/L	400	400	400	400	400	400
Porosity	0.42	0.41	0.41	0.42	0.41	0.41
Transmissivity, cm^2/d	39.12	50.31	14.51	39.12	50.31	14.51
Hydraulic Conductivity, cm/d	15.65	20.12	5.80	15.65	20.12	5.80
Retardation Factor, -	1.08	1.11	1.05	1.07	1.10	1.05

Solute (i.e., nitrate) dispersivities in each column experiment could further be explored from the BTCs presented in **Figure 6** and results are tabulated in **Table 4**. Dispersivities are sorted from high to low as follows: 4.53, 2.41, and 2.32 cm from soils S8, S2, and S3, respectively. Our transport experiments suggested that porous media with bigger grain size corresponded with higher dispersivities, perhaps due to the higher hydrodynamic dispersion coefficient generally associating with water flowing through coarser sands. The higher hydrodynamic dispersion coefficient could further lead to higher longitudinal dispersivities following **Equation 3** proposed by **Fetter et al. (1999)**.

$$\alpha_L = \frac{D_l}{v} \tag{3}$$

where $\boldsymbol{\alpha_L}$ is Dispersivity (L)
$\boldsymbol{D_l}$ is Hydrodynamic dispersion coefficient
$\boldsymbol{v}$ is Pore velocity

Nitrate BTCs from 3 experiments with 3 soil sub-classes (S2, S3, and S8) were simulated using MT3D model based on hydrodynamic input parameters obtained from column transport experiments tabulated in Table 3. The flow and transport domain was designed to mimic the real 1-D porous media column and divided into 20 grid cells as depicted in **Figure 7**.

Simulated nitrate BTCs provided by MT3D are illustrated and compared with observed BTCs from laboratory-scaled experiments in **Figure 6**. The simulated BTCs seemed to match fairly well with the observed data for all soil samples at both high and low flow rates, especially the normalized peak concentration, time to peak, and even the early arrival of BTCs. The longitudinal dispersivities were calculated from simulated BTCs, and the results are tabulated in **Table 2**. Longitudinal dispersivities generated by MT3D were fairly closed to the values obtained directly from column experimental observations, resulting in overall satisfying modeling efforts to simulate laboratory-scaled nitrate transport behavior through saturated porous media.

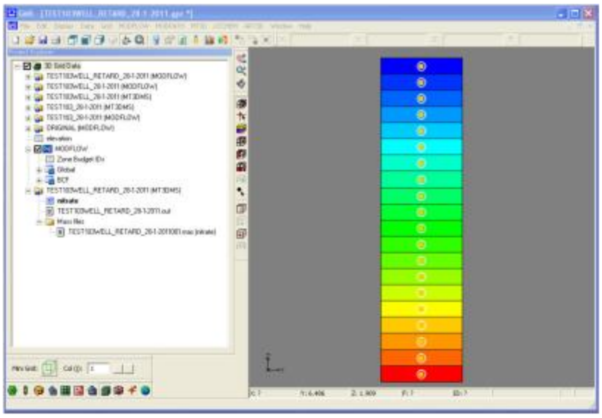

Figure 7. MT3D modeling domain and grid cells for 1D laboratory-scaled nitrate transport characteristics.

3.4 Field-scaled groundwater flow and nitrate transport characteristics and future prediction

Geology and hydrogeology of the study area can be classified based on the secondary data such as rock types and groundwater exploration bore logs obtained from Department of Mineral Resources (DMR) and Department of Groundwater Resources (DGR). Generally speaking, geology of the study area mostly comprises of terrain and colluviums deposit of Quaternary and Ordovician limestone. Two-layered aquifer system was constructed based on the hydrogeological setting of consolidated and unconsolidated materials. The first layer was composed of Permian Carbonate Aquifer (Pc), Colluvium (Qcl), and terrain deposit (Qt) units of unconsolidated aquifers. For the second layer, granite, Ordovician limestone (Ols), Silurian-Devonian Metamorphic (SDmm), and Permo-Carboniferus metasedimentary (PCms) were observed. Finite difference grid size of 50×50 m was constructed with grid refinement whenever necessary as shown in **Figure 8**.

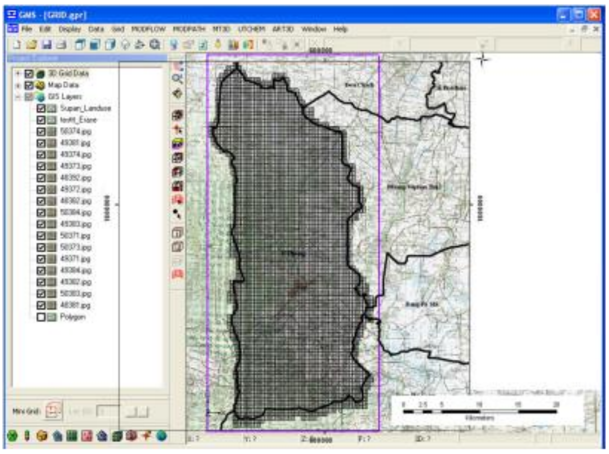

Figure 8. MT3D modeling domain and grid cells for field-scaled nitrate transport characteristics in Suphanburi.

The steady-state case in MODFLOW was adopted to simulate the regional groundwater conditions from field-scaled initial hydraulic conductivity values between 14.51-50.30 m^2/d obtained from steady-state pumping test data with groundwater recharge value of 1,059.90 mm/year (**DGR 2007**). Hydraulic conductivities, specific yield, and groundwater recharge were initially assigned based on available historical observed data and later adjusted during the calibration process. The calculated groundwater elevations and direction of groundwater flow were calibrated and verified with the previous water table records from 81 monitoring wells in the study area as shown in **Figure 9** with satisfying R^2 value of 0.97. Calibrated values of specific yield varied between 0.03 to 0.082 in the study area. Water table mapping indicated that flow in the aquifer was slow and mainly affected by surface topography, the thickness of saturated layer and variations in hydraulic conductivity.

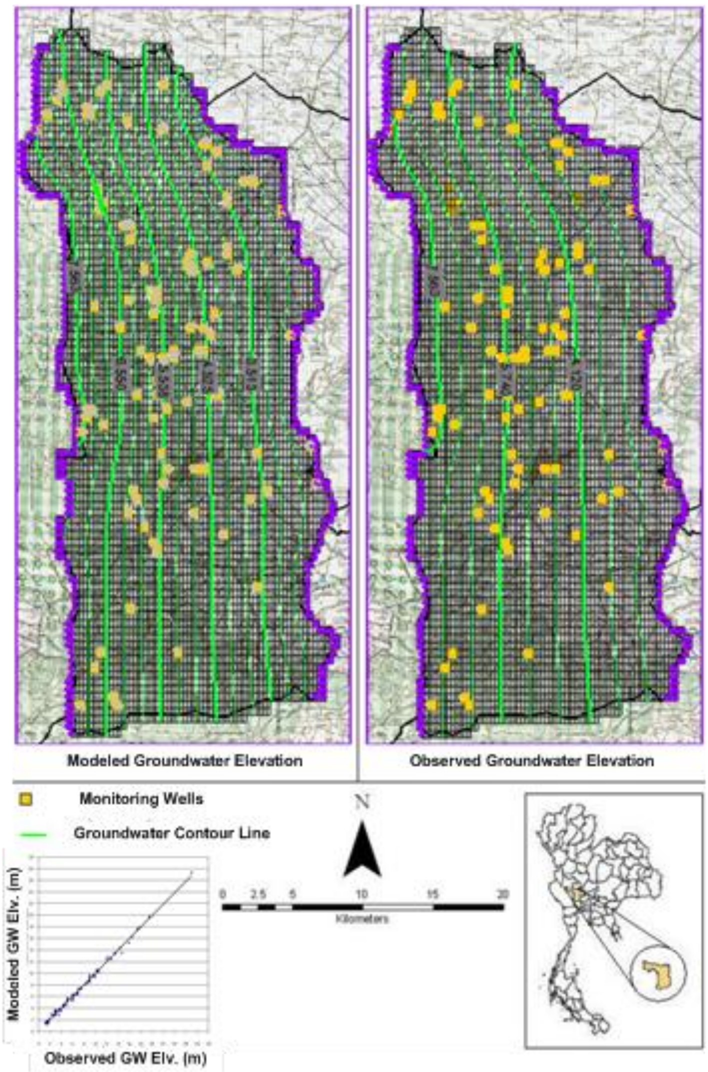

Figure 9. Regional groundwater flow simulation by MODFLOW in Suphanburi.

Solute transport model MT3D was simulated based on regional groundwater flow in MODFLOW with nitrate as a focus contaminant. Boundary conditions for the transport simulation were governed by regional flow characteristics from MODFLOW generation. Nitrate contamination case in Suphanburi as parts of the long-term monitoring program was employed as a proxy to evaluate DRASTIC vulnerability maps. Effective molecular diffusion coefficient and longitudinal dispersivity were upscaled based on laboratory-scaled column experimental results. Linear sorption isotherm was assumed with distribution coefficient of 0.0001 for the reaction term in MT3D. Initial effective porosity was applied to account for the actual velocity in advection term, and later was calibrated to yield the final values of 0.21-0.33. The model simulation was considered satisfying when the simulated nitrate concentrations were consistent with the observed data. **Figure 10** shows the linear regression of calibration results, in terms of scatter plots by comparing the observed nitrate concentration at monitoring wells to the calculated values from each grid cell.

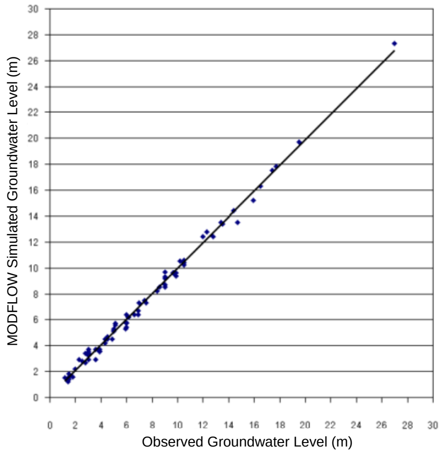

Figure 10. Scatter diagram of observed vs. simulated groundwater level.

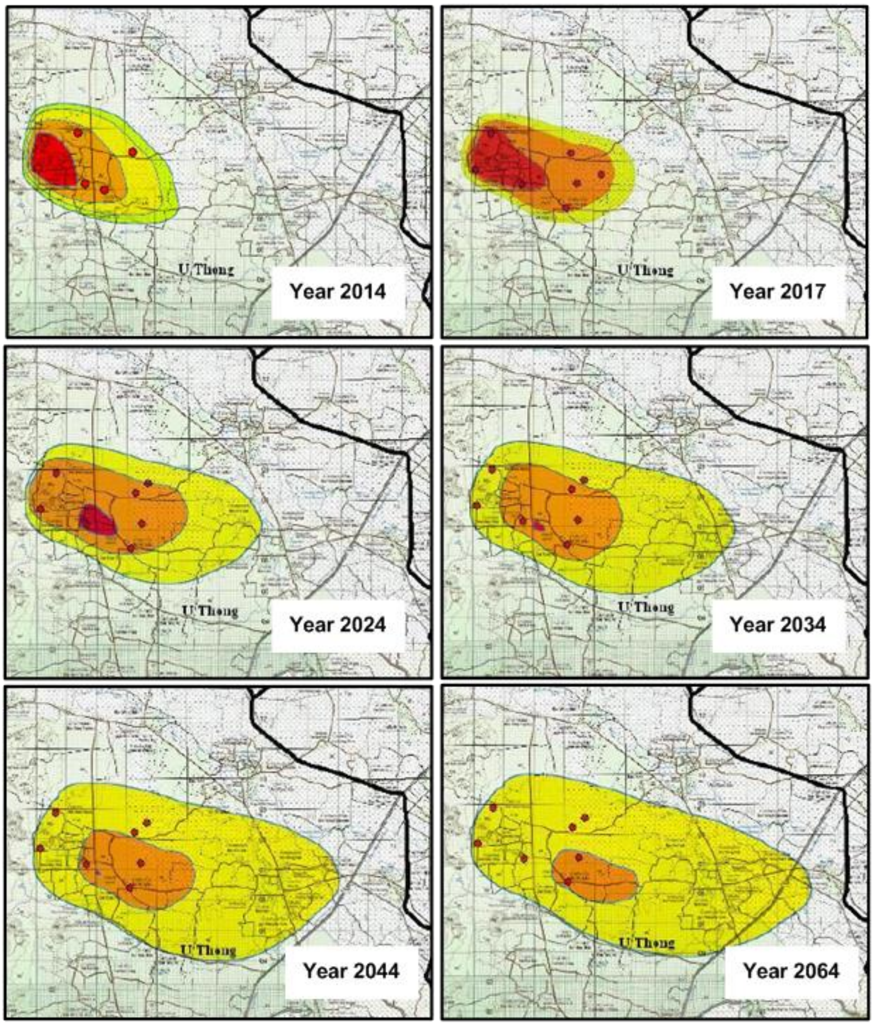

Figure 11. Extent of nitrate plume from MT3D model simulation in Suphanburi.

The calibrated model parameters were employed to predict the future response of groundwater flow and transport model for future scenarios. Mapping of predicted nitrate concentrations are illustrated in **Figure 10** and have been compared with nitrate distribution at the beginning of the simulation in 2014. Future development of nitrate plume migration in Suphanburi province were generated to simulate regional-scaled nitrate mobility in saturated groundwater aquifer under steady-flow conditions at 3, 5, 10, 20, 30, and 50 years as shown in **Figure 11**. Long-term future nitrate migration characteristics can be projected to improve effectiveness and efficiency of potential nitrate management and monitoring programs. The spatio-temporal distribution of nitrate concentration can be explained by the water quality in a given location depends not only on the agricultural and urban uses of the area directly overlying the study area, but also from the water quality inflowing from upstream. Moreover, nitrate concentrations in groundwater were seasonally dependent because of the increase in nitrate concentrations in rainy season due to higher agricultural activities and nitrogen fertilization.

4. CONCLUSIONS

In this study, the potential impact of nitrate distribution in groundwater is assessed. Suphanburi and Kanchanaburi were selected as our study areas due to the previous report on surface and subsurface nitrate contamination. Recent evidence from this study indicated that nitrate levels exceed the maximum contaminant level (MCL) of 45 mg/L in aquifer systems that underlie agriculture-dominated area with the maximum soluble nitrate concentration up to 158 mg/L near Muang and Southern Song-Pee-Nong districts. Nitrate hotspots were re-identified based on recent soil and groundwater quality assessment. 30% of shallow groundwater samples (< 30 m) were detected with higher nitrate concentration than MCL whereas only 23% of groundwater samples taken from >30 m deep were contaminated, suggesting the direct association of major nitrate contamination in groundwater aquifer with potential source above ground. Additionally, samples from various agricultural farmland collected and analyzed for nitrate concentration revealed that soil were heavily contaminated with nitrate from many areas associated with vegetable farming. Interestingly, our analysis shows that rice paddy fields generated relatively less excess nitrate in soil compared to area dedicated for vegetable farming. Sugarcane, the second most popular agricultural products grown in the study area, was associated with the second-highest nitrate concentration discovered in soil. A thorough understanding of the impact of nitrate contamination from agricultural activities was mandatory for better planning on fertilization practices at both local and regional scales.

Aqueous nitrate was significantly retarded by soil matrix, based on a slower migration of nitrate from the saturated packed soil column, especially when the system was operated at a lower flow rate. Important hydrodynamic properties governing transport of nitrate (i.e., retardation factor and longitudinal dispersivities) could be calculated from a series of column experiments conducted in this work and could further be employed in MODFLOW and MT3D models to simulate groundwater flow and nitrate transport at laboratory- and filed-scale. Longitudinal dispersivities generated by MT3D were fairly closed to the values obtained directly from column experiments, resulting in satisfying overall modeling efforts to simulate transport behavior of nitrate at the laboratory-scale. Future predictions of nitrate migration in Suphanburi province were generated to simulate nitrate transport at regional-scale as well as to simulate long-term future nitrate migration characteristics to improve effectiveness and efficiency of potential nitrate management and monitoring programs.

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