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Research Paper

Long-Term Monitoring And Modeling Extent Of Agricultural-Derived Nitrate Contamination In Shallow Groundwater Systems Of Thailand And Possible Links To Surficial Sources

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ABSTRACT

Undesirable chemical dissolution in groundwater can cause very serious health problems, whether the chemicals are naturally occurring or anthropogenic origin. In Thailand, soil and groundwater pollution has continued to increase due to population growth and agricultural development in the past decades. Nitrate contamination in groundwater has long been discovered in Thailand, arising from intensive agriculture with excessive fertilization. Contaminant transport modeling efforts in this paper were made to extend further long-term monitoring of nitrate contamination level in Suphanburi and Kanchanaburi and investigate any links of contaminant hotspots in groundwater with possible surface sources for further planning and management. Analysis of 160 groundwater samples collected from domestic and monitoring wells at various depths (100 samples from less than 30 m deep, and 60 samples from more than 30 m deep) for nitrogen (as NO_3^-), K, sulphate (as SO_4^{2-}) and other chemicals was carried out. Aqueous NO_3^- concentration levels in groundwater varied from as low as 0.18 to maximum of 151 mg/L (maximum concentration level = 45 mg/L; Ministry of Natural Resources and Environment Thailand).

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 the 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 stimulated 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

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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 usually result in non-point source pollution of groundwater and the effects of these practices accumulate with 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 an essential input for the 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 common agricultural contaminants found in the world's aquifers, and is present in relatively high concentrations in human and animal wastes (**Batlle Aguilar et al. 2007**).

Nitrate is well known for its highly water-soluble and can be easily transported through unsaturated soil to groundwater due to its negatively charged. In water, nitrate has no taste or scent and can only be detected through a chemical test. Naturally occurring concentrations of nitrate are generally less than 2 mg/L nitrate N. Many studies have shown high correlation and association between agriculture and nitrate concentration in groundwater (**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**). Long-term exposure to high nitrate levels in drinking water has been found in some studies to be a risk factor for several types of cancers including gastric, colorectal, bladder, urothelial and brain tumor (**CDPH 2013; Wolfe and Patz 2002**). 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, over the past few decades, the increase in population and advances made in farming technology has increased the demand for crops and livestock from agricultural industry and fertilizer consumption has continued rising since 2004 and reached its maximum of 167.1 kg/hectare of arable land in 2013. Nitrate accumulation in surface water and shallow groundwater of Thailand has been initially reported by **Asanachinda (1996)** who discovered high concentrations of nitrate, up to 290 mg/L, in groundwater collected from agricultural areas of Chiang Mai province in northern Thailand. Later on, nitrate contamination in groundwater suspected to be fertilizer-origin, has been identified in Suphanburi and Kanchanaburi based on 6 (out of 21) groundwater samples with maximum concentration level (MCL) higher than WHO drinking water standard of 50 mg/L 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 strong evidence of nitrate contamination in soil and groundwater, but also located the nitrate hotspot areas that can benefit for soil and/or groundwater pollution control, prevention, and monitoring programs.

From an 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 and Kanchanaburi due to the intensive agricultural activities with excess fertilization. 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) in the study area were collected and analyzed for nitrate (as NO_3^-), K, sulphate (as SO_4^{2-}) and other chemical parameters. Six column experiments were conducted using 3 representative porous media groups/subclasses under low and high flow conditions to explore the transport characteristics of aqueous nitrate. The numerical model in this study was developed based on a regional model of groundwater flow characteristics using the USGS 3D finite-difference code MODFLOW-2000 to simulate groundwater flow and groundwater head gradient distributions. The regional groundwater flow model was coupled with MT3D to simulate both laboratory- and regional-scaled nitrate transport characteristics using estimated and measured hydrogeological field parameters as well as to project long-term future nitrate migration characteristics. Future applications of the model can be used to test "what-if" scenarios to improve effectiveness and efficiency of potential nitrate management and monitoring programs.

2. Material and Methods

2.1 General Information of Suphanburi and Kanchanaburi Provinces

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 (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 depth.

Table 1 presents monthly average precipitation records in Suphanburi and Kanchanaburi from 1981-2020.

Month	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec
Suphanburi Rainfall (mm)	3.7	6.9	18.9	49.1	114.3	94.4	98.8	118.4	223.4	196.7	44.1	6.7
Kanchanaburi Rainfall (mm)	3.3	18.2	29.0	78.5	145.3	86.4	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 (**Fig.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 analyses 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 average rainfall data, groundwater recharge, and spatial concentration distribution of nitrate were processed in the ArcGIS environment.

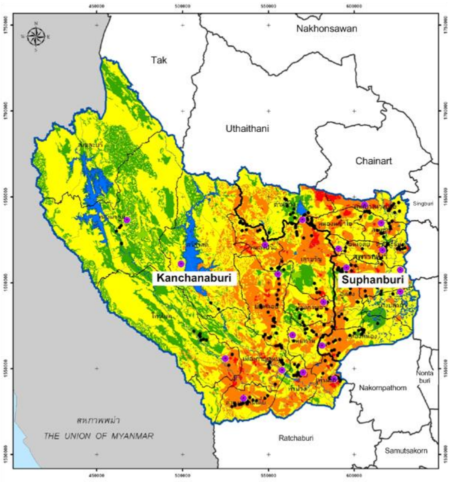

Fig. 1. Study Area Showing Groundwater Sampling Location

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 available (**Putthividhya and Pipitsomnat 2015**) were employed in a series of laboratory-scaled nitrate transport 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 rang in grain 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).

The column experimental setup is demonstrated in **Fig. 2**. 520 ppm NaCl solution was employed as a conservative tracer in these 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 the porous media container. The prepared soil sample was wet-packed into the clean column according to the procedure reported previously by **Putthividhya (2004)**. After packing, the column was flushed with Milli-Q water for at least 10 pore volumes (PV) at the designated flow rate, and followed by 520 ppm NaCl solution for 5 PV. Then, the column was flushed with 400 ppm nitrate solution through the column inlet for 5 PV. Steady-state effluents from the column were continuously collected using a fraction collector at column's outlet.

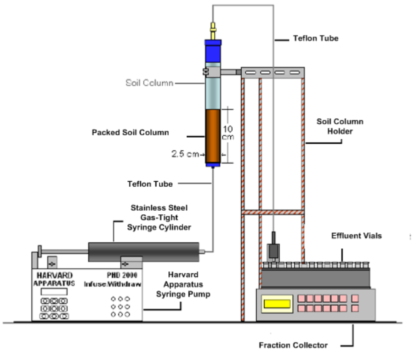

Fig. 2. Laboratory-Scaled Transport and Leaching Experimental Setup

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 groundflow 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 (**Bazargan-Lari et al. 2009**).

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

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 =head of groundwater
S_s =specific storage of aquifer materials
t =time

A block-centered 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 numerical models based on the partial differential equation at both laboratory- and field-scales. MT3D is a 3D solute transport model for simulation of advection, dispersion, and some chemical reactions of dissolved constituents in groundwater systems that can be described by the generalized partial differential equation describing the fate and transport of any contaminants of species ***k*** in 3D, transient groundwater flow systems can be formulated as shown in **Equation 2** (**Zheng 1990**).

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

Where,
C_k is the dissolved concentration of species ***k***
N is the porosity of the subsurface medium
T is the time
x_i is the distance along the respective coordinate axis
D_{ij} is the hydrodynamic dispersion coefficient tensor
V_{si} is the seepage or linear pore water velocity$=\frac{q}{}$ ()
q_s is the volumetric flow rate per unit volume of aquifer representing fluid sources (+) and sinks (-)
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. The hydraulic properties of the stratigraphic units were taken from Department of Groundwater Resources, Thailand. The true horizontal hydraulic conductivity was initially assumed to be 10 m/d for the silt-clay cap and it ranged among 50 and 100 m/d for the sand-gravel stratigraphic units. The vertical hydraulic conductivity was assumed to account for only 10% of the horizontal 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 verified with the observed dataset provided by DGR. 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.

Kanchanaburi province is located further in the west of Thailand approximately 250 km from Bangkok. Its elevation ranges from 140 to 1,046 m MSL with an average slope of 66%. Geology mainly composes of terrain and colluviums deposit of Quaternary and Ordovician limestone. Annual rainfall ranges from 1,250 to 1,940 mm with an average of 1,663 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 is from April to October and the rest of the year is considered dry.

3. Result and Discussions

3.1 *Nitrate in Groundwater*

The distribution of nitrate in groundwater in Suphanburi province was previously assessed (**Putthividhya and Pipitsombat 2015**). The results indicated that there were abundant of soluble nitrate detected in aquifer systems underneath Suphanburi. 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) and Kanchanaburi. The current spatial distribution of nitrate in groundwater was compared with the results previously examined and shown in **Fig. 3**.

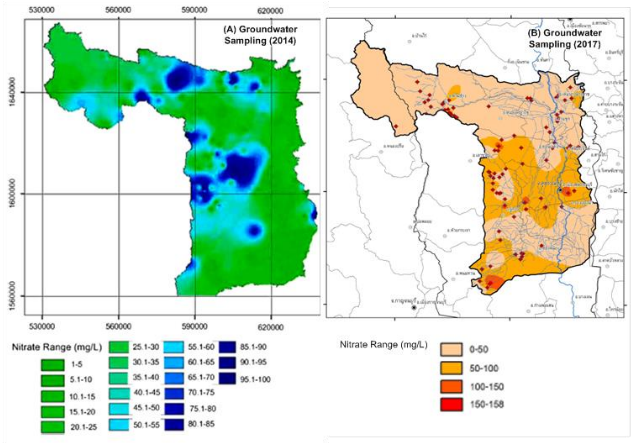

Fig. 3. Extent of the Spatial Soluble Nitrate Contamination in Groundwater in Suphanburi Province: (A) Data from Groundwater Sampling in 2014; an d(B) Data from Recent Groundwater Sampling in 2017.

Since naturally occurring nitrate concentrations are generally less than 2 mg/L nitrate N, nitrate concentration detected in the environment greater than 2 mg/L should be considered anthropogenic-origin. Using the nitrate MCL of 45 mg/L, the results in **Fig. 3** indicated that the extent of nitrate contamination in groundwater was expanding in 3 years time span (from 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 (north western 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 observed based on the investigation in this work near Muang and Southern Song-Pee-Nong Districts shown in **Fig. 3**.

Variation of nitrate concentrations in groundwater as a function of sampling depths is also presenting in **Fig. 4**. Groundwater samples were taken from municipal and monitoring wells in the study area, which could be divided into 2 groups, i.e., i) wells depth < 30 m; and ii) 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.

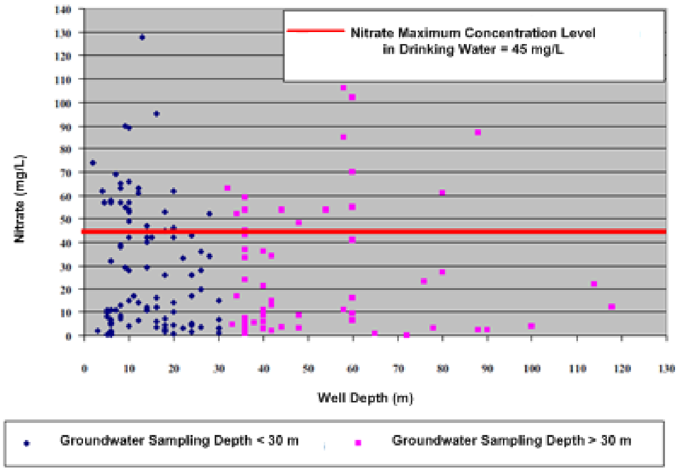

Fig. 4. Variation of Nitrate in Groundwater from Suphanburi and Kanchanaburi as a Function of Sampling Depths.

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 **Fig. 5** indicated that soil samples were heavily contaminated with nitrate from land directly associated with vegetable farming. The regional-scaled landuse 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 from Asparagus farming (**Tirado 2007**). Sugarcane, on the other hand, was the second most popular agricultural products grown in the study area with the secondly highest nitrate concentration discovered in 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 of Thailand.

3.3 Laboratory-Scaled Column Transport Experiments and Modeling Results

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. **Fig. 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 those of chloride (i.e., conservative tracer). 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.

The mean residence time of each column experiment could also be calculated from the BTCs as tabulated in **Table 2**. 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 soil 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 as well in **Table 2**. The retardation values 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.

Solute (i.e., nitrate) dispersivities in each column study could further be explored from the BTCs presented in **Fig. 6** and the results are tabulated in **Table 2**. 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 courser sands. The higher hydrodynamic dispersion coefficient could further result in higher longitudinal dispersivities following **Equation 2** proposed by **Fetter et al. (1999)**:

$$\alpha_L = \frac{D_l}{v} \tag{2}$$

where □*L* = Dispersivity (L)
D_l = Hydrodynamic Dispersion Coefficient
v = Pore Velocity (L/T)

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 the column transport experiments as 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 shown in **Fig. 7**.

Simulated nitrate BTCs provided by MT3D are depicted and compared with observed BTCs from laboratory-scaled experiments in **Fig. 6**. The simulated BTCs seemed to match fairly well with the observed data for all soil samples at both high and 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 disperivities 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.

Field-Scaled Groundwater Flow and Nitrate Transport Characteristics and Future Projection

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 **Fig. 8**.

The steady-state case in MODFLOW was adopted to simulate the regional groundwater condition using 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 were 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 **Fig. 9** with satisfying $\boldsymbol{R^2}$ 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.

Solute transport model MT3D was simulated based on regional groundwater flow in MODFLOW with nitrate as a focused 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 in the reaction term of MT3D model. 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 if the simulated nitrate concentrations were consistent with the observed data. **Fig. 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.

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 **Fig. 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 at 3, 5, 10, 20, 30, and 50 years as shown in **Fig. 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. Conclusion

Potential effects of nitrate on the quality of surface water and groundwater as well as the implications of such effects on human health (especially to children), pose issues of international concern that require science-based assessment and response. 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 secondly highest nitrate concentration discovered in soil. Nitrate in groundwater was evidently posing a public health risk for Thailand, and therefore was expedient to mitigate the impact of nitrate pollution in groundwater. 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 facto 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-scales. 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 projections of nitrate migration in Suphanburi province were generated to simulate nitrate transport at regional-scale as well as to project long-term future nitrate migration characteristics to improve effectiveness and efficiency of potential nitrate management and monitoring programs.

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