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Development of Field Pollutant Load Estimation Module and Linkage of QUAL2E with Watershed-Scale L-THIA ACN Model

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Abstract: The Long Term Hydrologic Impact Assessment (L-THIA) model was previously improved by incorporating direct runoff lag time and baseflow. However, the improved model, called the L-THIA asymptotic curve number (ACN) model cannot simulate pollutant loads from a watershed or instream water quality. In this study, a module for calculating pollutant loads from fields and through stream networks was developed, and the L-THIA ACN model was combined with the QUAL2E model (The enhanced stream water quality model) to predict instream water quality at a watershed scale. The new model (L-THIA ACN-WQ) was applied to two watersheds within the Korean total maximum daily loads management system. To evaluate the model, simulated results of total nitrogen (TN) and total phosphorus (TP) were compared with observed water quality data collected at eight-day intervals. Between simulated and observed data for TN pollutant loads in Dalcheon A watershed, the R^2 and Nash–Sutcliffe efficiency (NSE) were 0.81 and 0.79, respectively, and those for TP were 0.79 and 0.78, respectively. In the Pyungchang A watershed, the R^2 and NSE were 0.66 and 0.64, respectively, for TN and both statistics were 0.66 for TP, indicating that model performed satisfactorily for both watersheds. Thus, the L-THIA ACN-WQ model can accurately simulate streamflow, instream pollutant loads, and water quality.

Keywords: L-THIA ACN; pollutant loads; QUAL2E; simulation; TN; TP; water quality

1. Introduction

Estimation of pollutant loads in watersheds is very important for long-term watershed management plans such as non-point source (NPS) pollution management or total maximum daily loads (TMDLs) [1]. To estimate pollutant loads at a watershed, long-term monitoring of flow and water quality is essential. However, due to limitations in monitoring flow and pollutants in terms of labor and budget [2], various computer models have been developed and used worldwide [3–7]. Diverse input data are needed to operate complex watershed-scale hydrology or water quality models such as SWAT (Soil and Water Assessment Tool) [8], HSPF (Hydrologic Simulation Program–Fortran) [9], and SWMM (Storm Water Management Model) [10,11]. For this reason, simpler computer models, such as PLOAD (Pollutant Loading Application) [12], STEPL (Spreadsheet Tool for Estimating Pollutant Load [13,14],

and L-THIA (Long Term Hydrologic Impact Assessment) [15–18], have been used at the screening level. Among these models, L-THIA has been used in various studies and long-term watershed management plans because only daily rainfall data, in conjunction with a land use or soil dataset, are needed for daily direct runoff simulation and pollutant loads using the Natural Resources Conservation Services curve number (NRCS-CN) method and event mean concentration (EMC) databases for representative land uses [17,19–21]. The ArcView/ArcGIS/Web/Web GIS interface to the L-THIA model has been developed and used for almost two decades [15,16,18,20,22,23]. The Low Impact Development (LID) module was developed and integrated into L-THIA for environmentally friendly urban land use planning [24].

However, the current L-THIA model has limitations in estimating direct runoff during low-flow season because it does not compute direct runoff depending on the amount of rainfall [17,25,26]. In addition, the baseflow component for each hydrologic response unit (HRU) is not simulated [17]. When applying the L-THIA model to a watershed, lag time of the direct runoff component (to account for time needed to reach streams), the baseflow component contribution from unconfined aquifers, and flow routing through channel networks should all be considered. These limitations were addressed in the watershed-scale L-THIA asymptotic curve number (ACN) model developed by Ryu et al. [27].

With these capabilities enhanced, the watershed-scale L-THIA ACN model could be used at ungauged watersheds for streamflow estimation. However, it does not simulate pollutant loads from HRUs, or evaluate the effects of watershed routing on water quality changes through stream networks.

Thus, the objectives of this study are to (1) develop a module for estimation of pollutant loads from fields based on EMC databases for various land uses and amounts of rainfall; (2) to add the QUAL2E model (The enhanced stream water quality model) for stream water quality modeling to the watershed-based L-THIA model; and (3) to evaluate the accuracy of the watershed-scale L-THIA ACN model with water quality (watershed-scale L-THIA ACN-WQ model) by comparing estimated water quality with observed water quality.

2. Materials and Methods

2.1. Development of the Water Quality Simulation Module of the Watershed-Scale L-THIA ACN Model

The watershed-scale L-THIA ACN model, developed by Ryu et al. [27], does not include a water quality component. Therefore, a field pollutant load estimation module and a stream water quality module were added to the L-THIA model (Figure 1).

In the L-THIA model, pollutant loads for eight representative land uses were computed by multiplying EMC data collected in the USA by direct runoff volume [17,28].

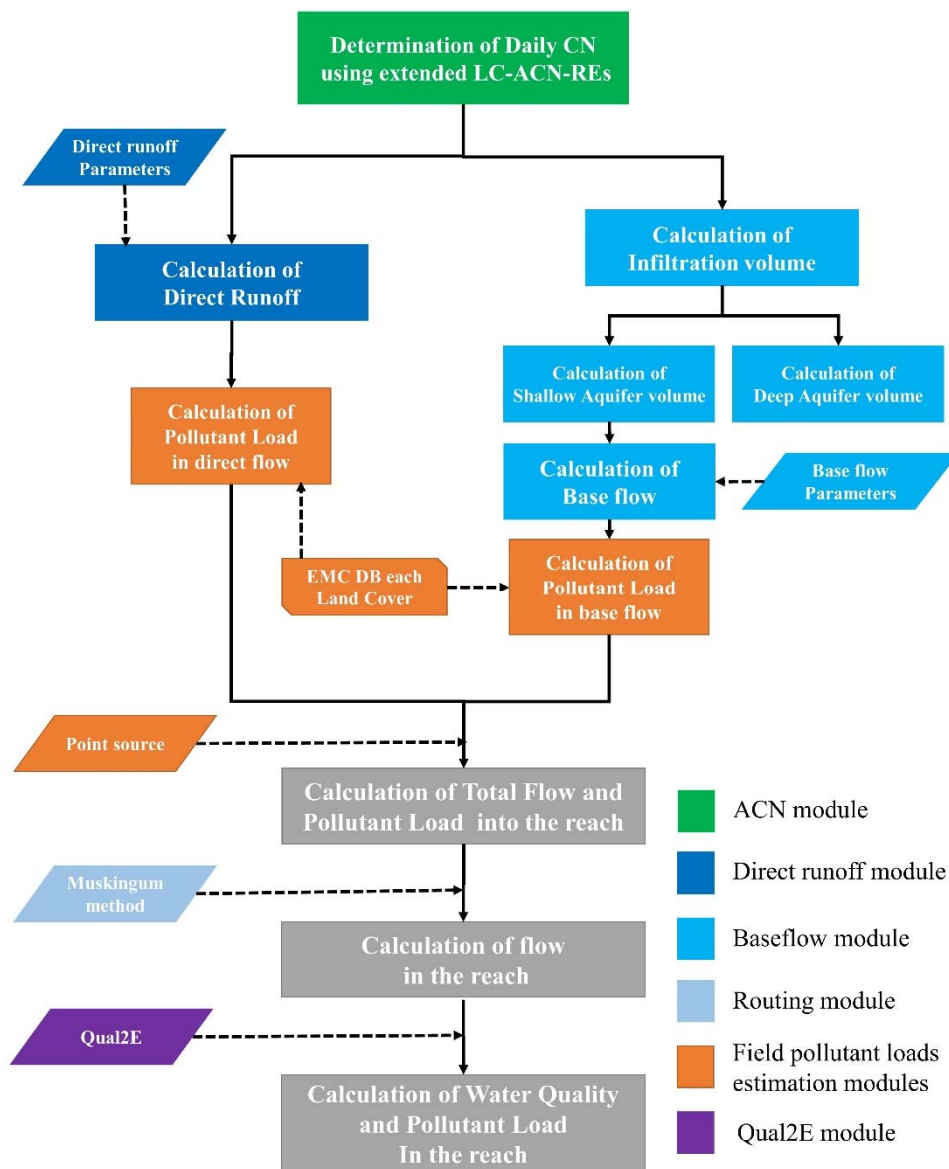


Figure 1. Flow diagram for development of watershed-scale L-THIA ACN-WQ (Long Term Hydrologic Impact Assessment Asymptotic Curve Number-Water Quality) model.

2.1.1. Development of the Field Pollutant Load Estimation Module

To develop the field pollutant load estimation module, it is assumed that pollutant loads through direct runoff and baseflow should be estimated from each HRU, and move to the stream of each subbasin. For this, the *EMC* data for direct runoff and baseflow components for various land cover types are needed. However, *EMC* data on infiltration from various land cover types are not available in South Korea, as is the case in many other countries. Thus, pollutant load from the baseflow component was estimated by multiplying the baseflow by adjusted *EMC* data. The adjusted *EMC* data is calculated by multiplying the *EMC* concentration by a user-defined coefficient to explain adsorption or degradation through soil and the loss of some portions to deep aquifers [29]. The *EMC* data were derived from monitoring data collected at various locations; thus, regional characteristics of *EMC* should be considered when these *EMC* data are applied. The *EMC* adjustment coefficients were used in pollutant estimation from each HRU in this study (Equation (1)), which allows ease of model use,

providing reasonable accuracy using a limited number of input parameters, similar to the original L-THIA model [15–18].

$$\begin{aligned} EMC_{DR} &= EMC \times Adj_EMC_{DR} \\ EMC_{BF} &= EMC \times Adj_EMC_{BF} \end{aligned} \quad (1)$$

where EMC_{DR} is the pollutant concentration in direct runoff (mg/L), EMC_{BF} is the pollutant concentration in baseflow (mg/L), EMC is the initial pollutant concentration of both direct runoff and baseflow (mg/L), Adj_EMC_{DR} is the adjustment coefficient for EMC in the direct runoff, and Adj_EMC_{BF} is the adjustment coefficient for EMC in the baseflow.

The pollutant loads through either direct runoff or baseflow from each HRU (Equation (2)) are summed together for each subbasin (Equation (3)) and then these loads, later converted to concentration of pollutants, are used as input data to the instream water quality simulation (Equation (4)):

$$\begin{aligned} L_{DR,hru} &= \left[\frac{EMC_{DR} \times Q_{DR,HRU}}{1000} \right] \\ L_{BF,hru} &= \left[\frac{EMC_{BF} \times Q_{BF,HRU}}{1000} \right] \end{aligned} \quad (2)$$

where $L_{DR,hru}$ is the pollutant load of direct runoff (kg), $L_{BF,hru}$ is the pollutant load of baseflow (kg), EMC_{DR} is the pollutant concentration in direct runoff (mg/L), EMC_{BF} is the pollution concentration in baseflow (mg/L), $Q_{DR,HRU}$ is the amount of direct runoff (m^3) discharged to the main channel, and $Q_{BF,HRU}$ the amount of baseflow (m^3) into the main channel:

$$\begin{aligned} L_{DR,sub} &= \sum_{HRU}^n L_{DR,hru} \\ L_{BF,sub} &= \sum_{HRU}^n L_{BF,hru} \end{aligned} \quad (3)$$

$$\begin{aligned} C_{DR,sub} &= \left[\frac{L_{DR,sub} \times 1000}{Q_{DR,sub}} \right] \\ C_{BF,sub} &= \left[\frac{L_{BF,sub} \times 1000}{Q_{BF,sub}} \right] \end{aligned} \quad (4)$$

where $L_{DR,sub}$ is the pollutant load of direct runoff in subbasin (kg), $L_{BF,sub}$ is the pollutant load of baseflow in subbasin (kg), C_{DR} is the pollutant concentration of direct runoff in the subbasin (mg/L), C_{BF} is the pollutant concentration of baseflow in the subbasin (mg/L), $Q_{DR,sub}$ is the amount of direct runoff discharged to the streams in the subbasin (m^3), and $Q_{BF,sub}$ is the amount of baseflow into the main channel in the subbasin (m^3).

The EMC data from the “Project of the long-term monitoring for the nonpoint source (NPS) pollution”, monitored by the Ministry of Environment (MOE) in South Korea, were used (Table 1) because the EMC data for various land cover types and rainfall ranges are available in these datasets. The NPS pollution loads have been measured over seven years (2008–2015) in a small subbasin for thirteen representative land covers. The data compiled through this long-term monitoring project have information on NPS pollution, such as the amount and ratio of NPS pollution in runoff, and EMC data [30–33]. In recent years, the MOE of Korea has determined the EMC and unit loads for each land cover using the 7-year data from the project. The data were validated through government hearings [34].

Table 1. Monitored event mean concentration (mg/L) of individual land cover for various rainfall magnitudes.

Land Cover	BOD ₅ (Biochemical Oxygen Demand)				TN (Total Nitrogen)				TP (Total Phosphorous)			
	<10 mm	10–30	31–50	>50 mm	<10 mm	10–30	31–50	>50 mm	<10 mm	10–30	31–50	>50 mm
Residential area	6.48	6.66	4.66	3.08	5.44	5.71	3.17	4.06	0.373	0.289	0.210	0.282
Manufacturing area	24.96	22.36	10.72	4.97	3.11	3.49	7.09	2.94	0.342	0.423	0.338	0.358
Regional public facility area	32.21	49.52	22.70	14.52	7.14	8.62	6.08	2.47	0.823	0.757	0.425	0.287
Recreational facility area	18.53	10.76	10.21	6.38	6.28	3.69	4.89	1.67	0.845	0.352	0.460	0.269
Road	10.61	7.17	8.89	3.31	6.18	2.68	2.76	2.01	0.221	0.231	0.217	0.176
Commercial area	6.52	8.12	4.48	4.12	5.81	5.12	2.59	5.68	0.277	0.331	0.212	0.453
Upland	2.26	3.40	3.57	3.50	2.38	2.83	2.33	2.41	0.215	0.386	0.301	0.436
Orchard	0.00	0.68	5.11	11.37	0.00	1.93	6.75	6.89	0.000	0.692	1.358	2.233
Green house	4.77	7.13	6.34	5.78	1.88	3.04	5.18	3.12	0.585	1.155	2.948	2.595
Paddy	0.00	1.10	2.09	2.63	0.00	1.41	3.88	5.54	0.000	0.154	0.423	0.962
Pasture	1.18	1.16	1.22	1.64	1.33	2.26	2.48	2.81	0.043	0.059	0.046	0.061
Forest	3.80	5.01	3.46	3.23	1.69	2.69	2.30	3.33	0.193	0.325	0.232	0.372
Bare land	6.52	8.12	4.48	4.12	5.81	5.12	2.59	5.68	0.277	0.331	0.212	0.453

2.1.2. Incorporation of Simplified QUAL2E Instream Water Quality Model

In this study, the simplified QUAL2E model [35], which has been widely used in one-dimensional water quality simulation, was added into the channel routing module of the watershed-scale L-THIA ACN model. The mechanism of instream water quality changes in the QUAL2E model is given in Brown and Barnwell [35].

To simulate water quality through stream networks using the simplified QUAL2E, flow and pollutant concentration parameters from each subbasin must be prepared. Pollutant concentrations calculated in Section 2.1.1 were classified as total nitrogen (TN) and total phosphorus (TP), without being further divided into specific categories such as nitrate nitrogen ($\text{NO}_3\text{-N}$), nitrite nitrogen ($\text{NO}_2\text{-N}$), ammonia nitrogen ($\text{NH}_3\text{-N}$), organic nitrogen (organic-N), organic phosphorus (organic-P), and inorganic-phosphorus (inorganic-P). However, for simulation of instream water quality changes, division into these categories is required.

Thus, pollutant concentrations of TN and TP in both direct runoff and baseflow were subdivided by partitioning coefficient parameters, which must be prepared by model users based on water quality data collected in the study watershed or nearby areas. After partitioning TN and TP, the six pollutant concentrations ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$, organic-N, organic-P and inorganic-P) of the subbasin, and of the direct runoff and baseflow, were used as input data for water quality simulation in streams, using the method in Brown and Barnwell [23]. For the baseflow component, organic-N and organic-P were excluded because these nutrients have greater adsorption characteristics to soil particles while moving downwards from the surface. Only soluble pollutants can infiltrate into aquifers from the land surface [29]. The QUAL2E model can only simulate carbonaceous biochemical oxygen demand (CBOD), and not bottle BOD_5 (five-day biochemical oxygen demand); therefore, bottle BOD_5 of the subbasin calculated by Equation (4) was converted to CBOD following Equation (5):

$$CBOD_u = \frac{\text{bottle}BOD_5 - 4.57(\text{NH}_3)(1 - e^{-5 \times knb}) - \alpha_4 A(1 - e^{-5 \times \rho})}{1 - e^{-5 \times kdb}} \quad (5)$$

where $CBOD_u$ is the ultimate CBOD concentration (mg/L), hereinafter referred as CBOD, and $\text{bottle}BOD_5$ is the bottle BOD_5 concentration calculated by Section 2.1.1 (mg/L), NH_3 is the ammonia concentration (mg/L), A is the algal biomass (mg/L), ρ is the respiration rate of algae (day^{-1}), knb is the nitrification rate coefficient in bottle BOD_5 at 20°C (day^{-1}), and kdb is the deoxidation rate coefficient in bottle BOD_5 at 20°C (day^{-1}).

Since initial dissolved oxygen (DO) and algae pollutant concentrations required in QUAL2E are not available in the EMC databases (Table 1), the initial concentration of DO was estimated using the method proposed by APHA (Washington, DC, USA) [36]. Changes in DO were calculated using the method in Brown and Barnwell [35]. The amount of algal biomass is closely related to chlorophyll *a* and can be derived by using its relationship with the concentration of chlorophyll *a* [37]. Chlorophyll *a* concentration was derived by using a simplified version of the exponential function proposed by Cluis et al. [37] (Equation (5)):

$$\begin{aligned} Chl &= 0, \text{ if } Q_{DR,sub} < 10^{-5} \text{ m}^3/\text{s}, \text{ or } (TP \text{ and } TN < 10^{-6}) \\ Chl &= \frac{0.5 \times 10^{2.7}}{Q_{DR,sub}}, \text{ if } Q_{DR,sub} > 10^{-5} \text{ m}^3/\text{s}, \text{ and } (TP \text{ and } TN > 10^{-6}) \\ Chl &= \frac{0.5 \times 10^{0.5}}{Q_{DR,sub}}, \text{ if } Q_{DR,sub} > 10^{-5} \text{ m}^3/\text{s}, TP < 10^{-6} \text{ and } TN > 10^{-6} \end{aligned} \quad (6)$$

where Chl is the chlorophyll *a* concentration in the direct runoff ($\mu\text{g/L}$), $Q_{DR,sub}$ is direct runoff flow rate into the main channel (m^3/s), TN is the total Kjeldahl nitrogen load (kmol), TP is the total phosphorus load (kmol).

The initial concentration of DO was estimated using Equation (7) proposed by APHA (Washington, DC, USA) [36]:

$$DO = \exp \left[-139.34410 + \frac{1.575701 \times 10^5}{TempK} - \frac{6.642308 \times 10^7}{TempK^2} + \frac{1.243800 \times 10^{10}}{TempK^3} - \frac{8.621949 \times 10^{11}}{TempK^4} \right] \quad (7)$$

where DO is the saturation concentration of dissolved oxygen (mg/L), and *TempK* is water temperature in Kelvin (273.15 + °C).

Water temperature was calculated using Equation (8) proposed by Stefan and Preud'homme [38]:

$$TempK = 273.15 + (5.0 + 0.75T_{average}) \quad (8)$$

where *TempK* is water temperature during the day (°C) and *T_{average}* is the average air temperature during the day (°C).

The initial concentrations of chlorophyll *a* and DO in the subbasin were used for input data of the instream water quality component of the watershed-scale L-THIA ACN-WQ model. The mechanism of instream water quality changes in the QUAL2E model is shown in Figure 2. More detailed description for each submodule of QUAL2E is explained below in details.

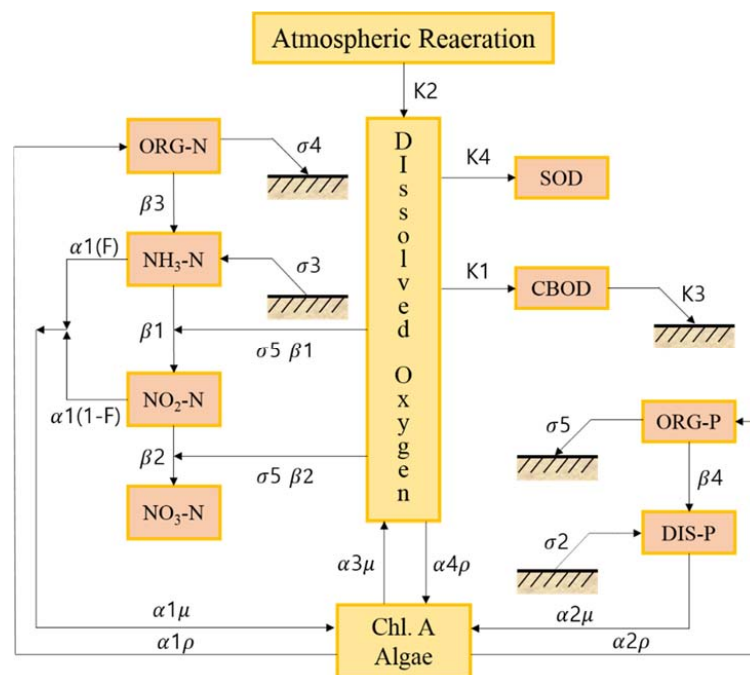


Figure 2. General structure of QUAL2E [35].

Weather data (e.g., solar radiation, duration of solar radiation and average air temperature) are required to simulate instream water quality changes using QUAL2E. A change in algae biomass in streams affects nutrient levels. The amount of algal biomass is simulated using solar radiation and duration as outlined by Brown and Barnwell [35]. The watershed-scale L-THIA ACN-WQ model was modified to use the weather data for instream water quality simulation.

In the watershed-scale L-THIA ACN-WQ model, the EMC data can be adjusted to consider local EMC characteristics. The subdivisions of TN and TP were added to the model to simulate the NO₃-N, NO₂-N, NH₃-N, organic-P and inorganic-P in streams (Table 2).

Pollutant loads in the stream were simulated using the QUAL2E model and the parameters in QUAL2E were used in the watershed-scale L-THIA ACN-WQ model (Table 3). The default values of QUAL2E parameters were set in the model, as shown in Table 3, with reference to studies of Glavan et al. and Na [39,40].

Table 2. Description of event mean concentration (EMC), nitrogen, and phosphorus parameters used in instream water quality module.

Parameter Name	Description	Range	Default Value
<i>Adj_EMCDR,N</i>	Constant value for adjustment of nitrogen in surface	−0.9–0.9	1.0
<i>Adj_EMCBF,N</i>	Constant value for adjustment of nitrogen in aquifer	−0.9–0.9	1.0
<i>Adj_EMCDR,P</i>	Constant value for adjustment of phosphorus in surface	−0.9–0.9	1.0
<i>Adj_EMCBF,P</i>	Constant value for adjustment of phosphorus in aquifer	−0.9–0.9	1.0
TN_ratio1 ¹	Ratio of organic-N in total nitrogen	0.0–0.9	0.05
TN_ratio2 ¹	Ratio of NO ₃ -N in total nitrogen	0.0–0.9	0.8
TN_ratio3 ¹	Ratio of NH ₃ -N in total nitrogen	0.0–0.9	0.1
TP_ratio1 ²	Ratio of organic-P in total phosphorus	0.0–0.9	0.5

Notes: ¹ Ratio of NO₂-N = 1 – (Sum of TN_ratio1, TN_ratio2 and TN_ratio3); ² Ratio of dissolved P = 1 – TP_ratio1.

Table 3. Description of QUAL2E parameters used in instream water quality module.

Parameter Name	Description	Recommended Range in QUAL2E	Default Value
RS1	Local algal settling rate in the reach at 20 °C	0.15–1.82	0.3408
RS2	Benthic source rate for dissolved phosphorus in the reach at 20 °C	0.001–0.1	0.1
RS3	Benthic source rate for NH ₄ -N in the reach at 20 °C	0.0–1.0	0.0
RS4	Rate coefficient for organic nitrogen settling in the reach at 20 °C	0.001–0.1	0.001
RS5	Organic phosphorus settling rate in the reach at 20 °C	0.001–0.1	0.08
RK1	Carbonaceous biological oxygen demand (CBOD) deoxygenation rate coefficient in the reach at 20 °C	0.02–3.4	0.3
RK2	Oxygen reaeration rate in accordance with Fickian diffusion in the reach at 20 °C	0.0–100.0	1.0
RK3	Rate of loss of CBOD due to settling in the reach at 20 °C	−0.36–0.36	−0.36
RK4	Benthic oxygen demand rate in the reach at 20 °C	0.0–100.0	0.0
BC1	Rate constant for biological oxidation of NH ₄ to NO ₂ in the reach at 20 °C	0.1–1	0.1
BC2	Rate constant for biological oxidation of NO ₂ to NO ₃ in the reach at 20 °C	0.2–2	0.2
BC3	Rate constant for hydrolysis of organic N to NH ₄ in the reach at 20 °C	0.2–0.4	0.03
BC4	Rate constant for mineralization of organic P to dissolved P in the reach at 20 °C	0.01–0.7	0.1
RTH	Algal respiration rate at 20 °C	0.05–5.0	0.05
TFAC	Fraction of photosynthetically active solar radiation	0.0–1.0	0
MMX	Maximum specific algal growth rate at 20 °C	1.0–3.0	1.0
IG	QUAL2E algae growth limiting option (1: multiplicative, 2: limiting nutrient, 3: harmonic mean)	1, 2, 3	1
A0	Ratio of chlorophyll- <i>a</i> to algal biomass	10.0–100.0	10
A1	Fraction of nitrogen algal biomass	0.07–0.09	0.071
A2	Fraction of phosphorus algal biomass	0.01–0.02	0.003
A3	Rate of oxygen production per unit of algal photosynthesis	1.4–2.3	1.4
A4	Rate of oxygen uptake per unit of algal respiration	1.6–2.3	1.6
A5	Rate of oxygen uptake per unit NH ₃ -N oxidation	3.0–4.0	3.0
A6	Rate of oxygen uptake per unit NO ₂ -N oxidation	1.0–1.14	1.0
Lam0	Non-algal portion of the light extinction coefficient	0–10	0
Lam1	Linear algal self-shading coefficient	0.006–0.065	0.006
Lam2	Nonlinear algal self-shading coefficient	0–1	0
KN	Michaelis-Menten nitrogen half-saturation constant	0.01–0.3	0.01
KP	Michaelis-Menten phosphorus half-saturation constant	0.001–0.05	0.001
KL	Light half-saturation coefficient	0.223–1.135	0.223
Knb	Nitrification rate coefficient in CBOD ₅	–	0.5
Kdb	Deoxidation rate coefficient in CBOD ₅	–	0.5
PN	Preference factor for ammonium nitrogen	0.0–1.0	0.0

2.2. Applications of the Watershed-Scale L-THIA ACN-WQ Model

To evaluate the watershed-scale L-THIA ACN-WQ model, estimated streamflow and pollutant loads were compared with observed data at two study watersheds (Dalcheon A and Pyungchang A in South Korea where the TMDL was carried out; Figure 3).

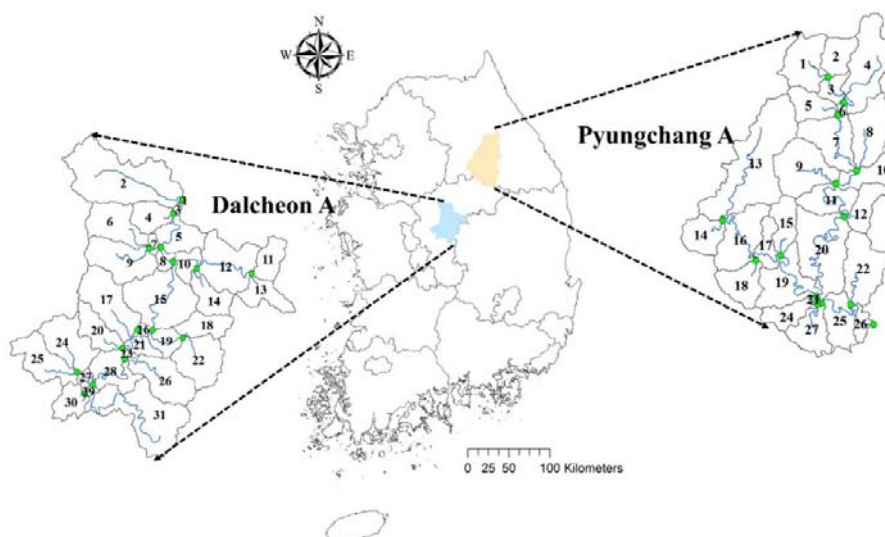


Figure 3. Two study watersheds used for evaluation of watershed-scale L-THIA ACN-WQ model.

Dalcheon A is located in the Han River basin in South Korea. The average slope of this watershed (22.0%) is lower than that of Pyungchang A watershed (30.8%). Land cover types in Dalcheon A consist of forest (71.9%), agricultural (18.6%), urban (2.5%), bare land (0.9%) and others (6.1%).

Pyungchang A is also located in the Han-River basin. The land cover types consist of forest (80.5%), agricultural (12.8%), urban (1.7%), bare land (2.0%), and others (1.2%).

Information on the study watersheds including surface area, soil, climate, agriculture production type and water quality information are shown in Table 4.

Table 4. Information of the study area.

Information of Study Area		Dalcheon A	Pyungchang A
Surface area (km ²)		1200.33	1756.87
Average precipitation (2011–2014) (mm/year)		1315.6	1389.6
Average temperature (2011–2014) (degree)		11.7	12.8
Hydrologic soil group (%)	A	11.8	11.7
	B	16.0	15.9
	C	36.6	35.8
	D	35.6	36.6
Agriculture production type (%)	Upland crop	42.5	32.6
	Green house	14.7	20.7
	Ochard	21.6	22.6
	Paddy	21.2	24.1
Average water quality (2011–2014) (mg/L)	BOD	0.96	0.88
	TN	2.76	2.91
	TP	0.02	0.03

The watershed-scale L-THIA ACN-WQ model, which can estimate instream water quality, was applied to these study watersheds for the period 2010–2014. The hydrology model parameters and water quality-related parameters were calibrated using 8-day interval observed flow and water quality data (the only flow and water quality data available for these TMDL watersheds).

In addition to the adjusted *EMC*, various QUAL2E parameters such as algal respiration rate, algal settling rate, algal growth rate, nitrification rate of nitrite, and phosphorus settling rate were adjusted for a better fit with measured TN and TP data, when calibrating instream water quality of TN and TP.

3. Results and Discussion

3.1. Estimation of Pollutant Load

For assessing the model performance, parameters of the model were manually calibrated by comparing model simulations with observations for streamflow, TN, and TP. Pearson coefficient of correlation (R^2) and Nash–Sutcliffe simulation efficiency index (*NSE*) [41] were used as the objective function, all of which are well known and generally used in evaluating the performance of models [39,42].

The calibrated CN values in Dalcheon A and Pyungchang A are 3% lower and 9% higher, respectively, than the default CN values (Table 5). The calibrated value for field slope length at Dalcheon A watershed is 1.5 times greater than that estimated from the relationship between average slope and slope length suggested by Wischmeier and Smith [43].

Table 5. Calibration parameters for streamflow component of the L-THIA ACN-WQ model.

Watershed	Adj_CN ¹	$SLSUB$ ²	DR_{lag} ³	α_{BF} ⁴	aqf_{thr} ⁵	Fr_{conf} ⁶	BF_{delay} ⁷	$Mk1$ ⁸	$Mk2$ ⁹	Mkx ¹⁰
Dalcheon A	0.03	1.5	4	0.7	20.0	0.10	1	0.05	0.95	0.2
Pyungchang A	0.09	1.0	8	0.5	30.0	0.05	5	0.25	0.75	0.5

Notes: ¹ Adjusted coefficient for CN; ² Adjustment for slope length; ³ Direct runoff lag coefficient; ⁴ Baseflow recession constant; ⁵ Threshold water level for baseflow contribution in the unconfined aquifer (mm); ⁶ Fraction of water flowing into confined aquifer; ⁷ Delay time in aquifer recharge following water infiltration at surface (day); ⁸ Weighting factor for influence of normal flow on storage time constant value; ⁹ Weighting factor for influence of low flow on storage time constant value; ¹⁰ Weighting factor for Muskingum method.

Threshold water levels (aqf_{thr}) in Dalcheon A and Pyungchang A were 20 mm and 30 mm, respectively.

Calibrated parameters of the watershed-scale L-THIA ACN-WQ model indicate that *EMC* adjustment coefficients affect instream water quality as well as pollutant loads from each subbasin (Table 6). This indicates that the *EMC* should be adjusted to account for differences in agricultural management (fertilizer/manure application rates, tillage, etc.) or urban impervious areas and population density at each watershed.

As shown in the calibration result, *EMCs* can be different for direct runoff and baseflow, and they should be separately calibrated.

In many other countries, including South Korea, it is difficult to predict the *EMCs* for baseflow by individual land cover type.

Therefore, if the L-THIA ACN-WQ model is calibrated with the *EMC* for baseflow in areas with various land cover types, the representative *EMCs* for baseflow by individual land cover type could be estimated. Furthermore, the representative *EMCs* for baseflow could be used for estimating a representative ratio of baseflow pollution loads to streamflow pollution loads that can contribute to estimating pollutant loads for baseflow in ungauged watersheds.

The parameters of the partitioning coefficients of organic N, NO_3 -N, and NH_3 -N in TN and organic-P in TP were defined based on the ratio of measured water quality data from outlets in the study watersheds (Table 6). Organic-N, NO_3 -N, NH_3 -N, and organic P (thus inorganic P) ratio values are similar in both watersheds, while NO_2 -N concentrations are different. Thus, these partitioning values (organic-N, NO_3 -N, NH_3 -N, and organic P) from observed data were used as model inputs for both study watersheds, while these could be adjusted or calibrated based on local flow and water

quality conditions. If no observed water quality data are available, these partitioning model parameters could be calibrated to reflect local conditions indirectly. Parameters related to water quality in streams (e.g., respiration rate of algae, growth rate of algae, settling rate for phosphorus, nitrification rate) were calibrated manually to better reflect stream characteristics.

Table 6. Calibration parameters for the water quality component of the L-THIA ACN-WQ model.

Parameters	Dalcheon A	Pyungchang A
<i>Adj_EMCD_{DR,N}</i>	0.80	0.70
<i>Adj_EMCD_{BF,N}</i>	0.90	0.90
<i>Adj_EMCD_{DR,P}</i>	0.60	0.40
<i>Adj_EMCD_{BF,P}</i>	0.40	0.35
TN_ratio1	0.03	0.03
TN_ratio2	0.95	0.95
TN_ratio3	0.01	0.01
TP_ratio1	0.40	0.40
RS1	1.00	1.00
RS2	0.001	0.001
RS3	0.001	0.01
RS4	0.10	0.001
RS5	0.10	0.1
RS6	2.50	2.50
RK1	0.50	0.50
RK2	50	50
RK3	0.36	0.36
RK4	2.00	2.00
RK5	2.00	2.00
RK6	1.71	1.71
BC1	0.10	0.55
BC2	0.20	2.00
BC3	0.02	0.4
BC4	0.01	0.01
TFAC	0.30	0.30
MMX	1	1
IG	3	3
A0	80	80
A1	0.09	0.09
A2	0.01	0.01
A3	1.60	1.60
A4	2	2
A5	3.50	3.50
A6	1.00	1.00
Lam0	1	1
Lam1	0.03	0.03
Lam2	0.054	0.054
KN	0.75	0.02
KP	0.020	0.025
KL	0.025	0.75
Knb	0.50	0.03
Kdb	0.03	0.045
PN	0.45	0.50

3.2. Model Performance Compared to Observed Streamflow And Pollutant Loads

Estimated average streamflow using the watershed-scale L-THIA ACN-WQ model and observed streamflow at Dalcheon A watershed were 27.68 m³/s and 26.29 m³/s, respectively. The *R*² and *NSE* values were 0.79 and 0.78, respectively (Table 7, Figure 4). Estimated average and observed streamflow at Pyungchang A watershed were 56.48 m³/s and 53.69 m³/s, respectively (Table 7, Figure 5).

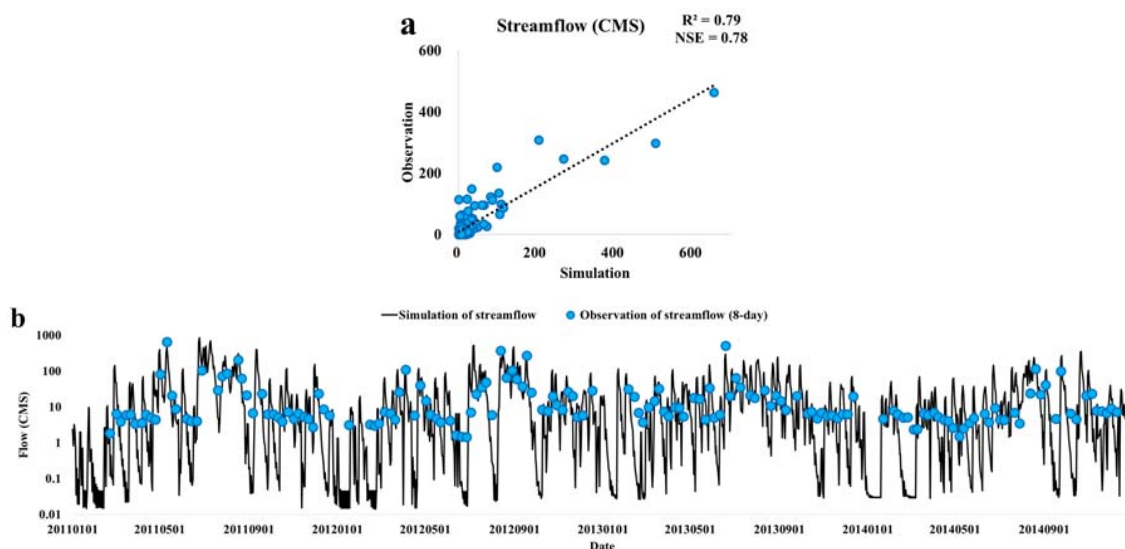


Figure 4. Comparison between simulated streamflow (a) and observed streamflow (b) at Dalcheon A watershed (2011–2014).

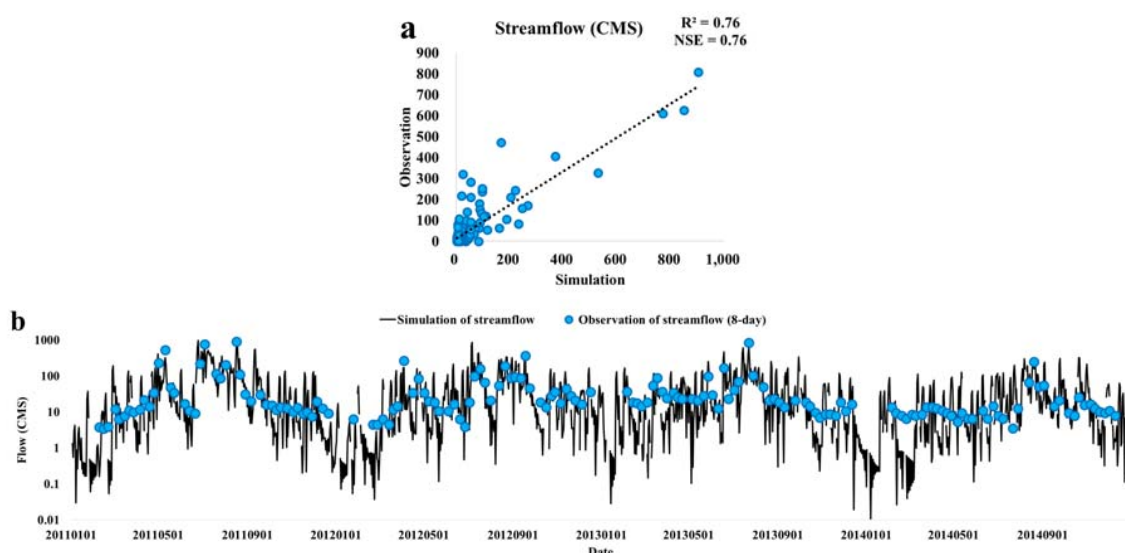


Figure 5. Comparison between simulated streamflow (a) and observed streamflow (b) at Pyungchang A watershed (2011–2014).

Table 7. Comparison between estimated and observed eight-day average streamflow in the period between 2011 and 2014.

Watershed	Average Streamflow (2011–2014) (m ³ /s)		R ²	NSE
	Observation	Estimation		
Dalcheon A	26.29	27.68	0.79	0.78
Pyungchang A	53.69	56.48	0.76	0.76

Average estimated and observed TN pollutant loads in Dalcheon A were 5227.04 kg and 6077.44 kg, respectively, (Table 8) and R² and NSE values were 0.74 and 0.72, respectively (Figure 6). Estimated and observed pollutant loads in Pyungchang A were 10,282.49 kg and 13,457.67 kg, respectively (Table 8). The R² and NSE values were 0.66 and 0.64, respectively (Figure 7).

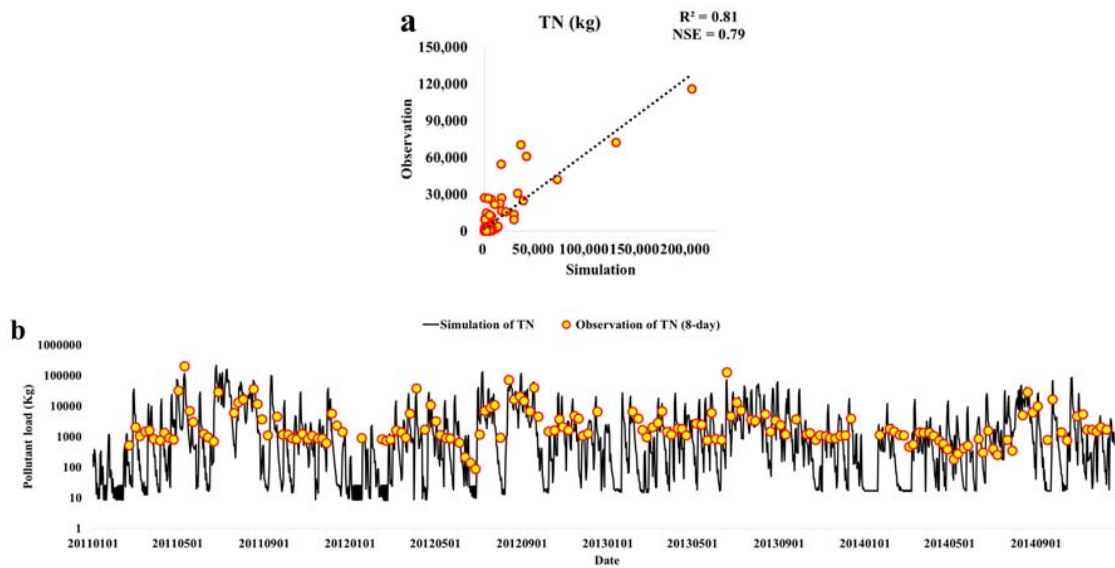


Figure 6. Comparison between simulated TN (a) and observed TN (b) at Dalcheon A watershed (2011–2014).

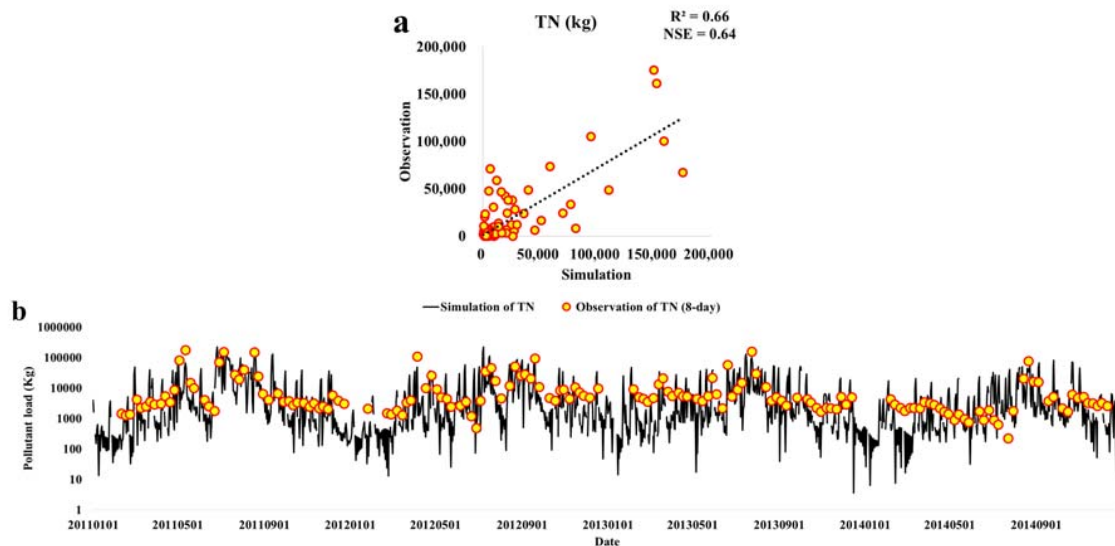


Figure 7. Comparison between simulated TN (a) and observed TN (b) at Pyungchang A watershed (2011–2014).

Table 8. Comparison between estimated and observed eight-day average pollutant loads in the period between 2011 and 2014.

Watershed	Pollutant Loads	Average Pollutant Load (2011–2014) (kg)		R^2	NSE	Average Concentration (2011–2014) (mg/L)	
		Observation	Estimation			Observation	Estimation
Dalcheon A	TN	6077.44	5227.04	0.81	0.79	2.76	2.70
	TP	242.13	195.75	0.79	0.78	0.02	0.03
Pyungchang A	TN	134,57.67	10,282.49	0.66	0.64	2.91	2.35
	TP	302.51	306.02	0.66	0.66	0.03	0.04

Average estimated and observed TP pollutant loads in Dalcheon A were 195.75 kg and 242.13 kg, respectively. R^2 and NSE values were 0.70 and 0.64. Average pollutant loads estimated and observed in Pyungchang A were 306.02 kg and 302.51 kg. The R^2 and NSE values were both 0.66 (Table 8, Figures 8 and 9).

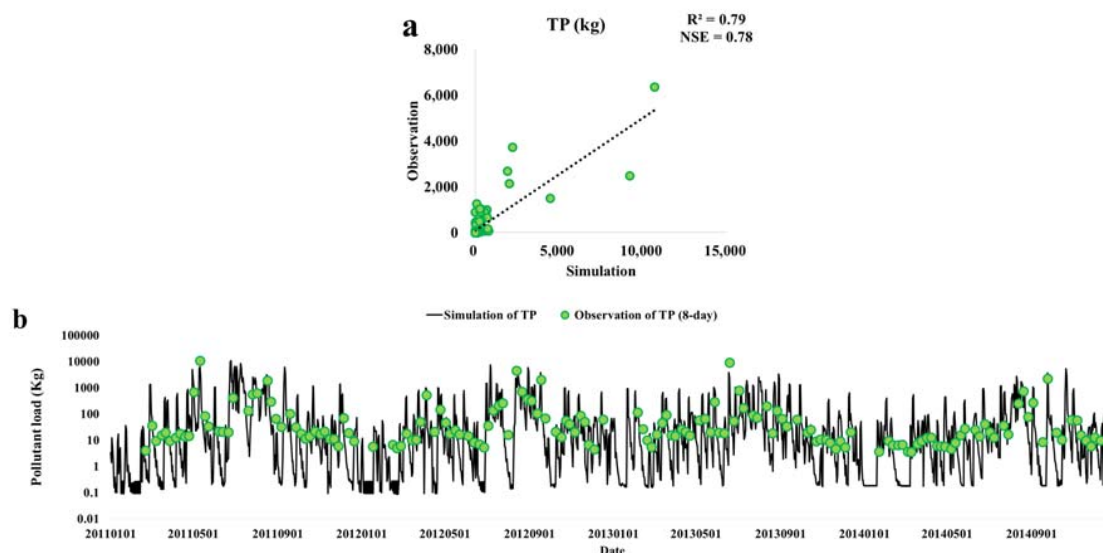


Figure 8. Comparison between simulated and observed TP at Dalcheon A watershed (2011–2014).

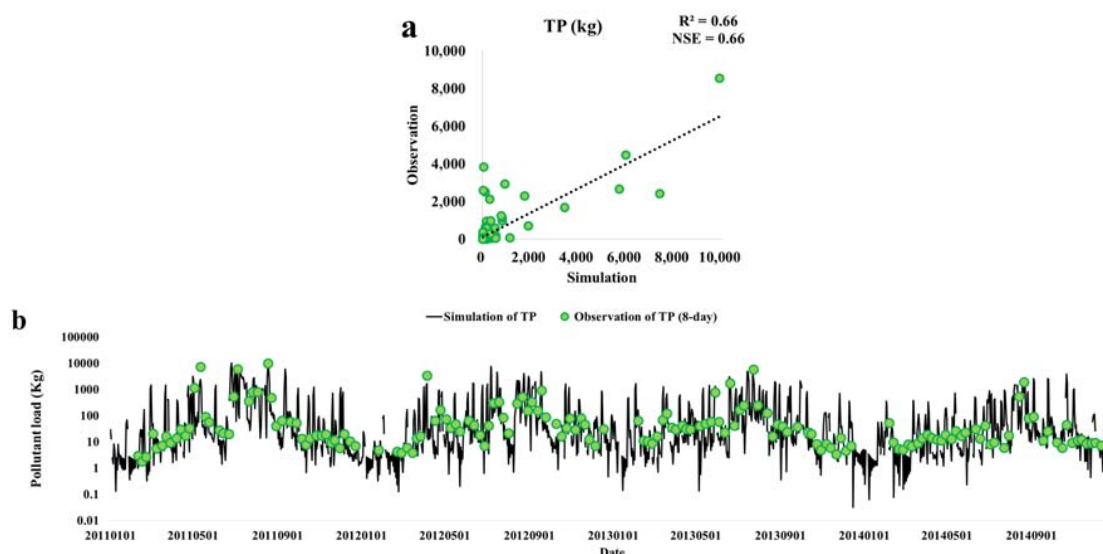


Figure 9. Comparison between simulated and observed TP at Pyungchang A watershed (2011–2014).

The simulated and observed data for concentrations of TN and TP match reasonably well. For Dalcheon A, estimated and observed TN concentration values were 2.70 mg/L and 2.76 mg/L, respectively (Table 8). TP estimated and observed values were 0.03 mg/L and 0.02 mg/L, respectively. For Pyungchang A watershed, average simulated and observed values were 2.35 and 2.91 mg/L of TN, and 0.04 and 0.03 mg/L of TP, respectively.

These results show that the watershed-scale L-THIA ACN-WQ model can simulate not only streamflow but also pollutant loads at a watershed with less input data required than for complex watershed-scale models.

4. Conclusions

In this study, the watershed-scale L-THIA ACN model, developed by Ryu et al. [27], was enhanced by developing a field pollutant load estimation module and incorporating the instream QUAL2E model, in order to simulate pollutant loads at a watershed scale. Comparison of the simulated results of this L-THIA ACN-WQ model with observed values from two watersheds in South Korea reveal that the model can simulate not only streamflow but also pollutant loads reasonably well [44,45].

Eight parameters used for calculating pollutant loads in each land cover and 33 parameters for water quality changes in streams were added in the model. The model requires 51 parameters (ten for streamflow, eight for pollutant loads from the watershed, and 33 for instream water quality—default values for these 33 parameters, recommended by the US EPA, are available) in order to simulate streamflow and water quality.

Based on the calibrated parameters, the default values of the 33 instream water quality parameters could be used at ungauged watersheds in conjunction with ten (for streamflow) and eight (for watershed pollutant loads) model parameters prepared according to the localized conditions of the watershed in question. Further evaluations of the watershed-scale L-THIA ACN-WQ model under different weather, land use, and soil conditions are needed.

This study attempted to improve the shortcomings of the existing L-THIA model, which could simulate only pollutant loads for direct runoff. The model suggested in this study can estimate the total instream pollutant loads and water quality considering baseflow as well as direct runoff.

Furthermore, existing watershed models such as SWAT or HSPF involve complex hydrologic components and many parameters related to the watershed characteristics [46]. Consequently, users need to spend lots of time and effort to calibrate various model parameters.

On the other hand, the L-THIA ACN-WQ model can successfully estimate the total streamflow (direct runoff and baseflow) and instream pollutant loads with less parameters than those of SWAT or HSPF. In addition, the operating time of models for long-term simulations is significantly reduced when compared to the other catchment models.

In this regard, we believe that the L-THIA ACN-WQ model can be a useful tool for simulating streamflow and water quality for sustainable watershed management plans.

Nevertheless, there are still limitations in the developed model in that sensitivity and uncertainty analysis should be manually conducted. Moreover, the model has no function for simulating other water qualities (e.g., suspended soil) excluding the BOD, TN, and TP.

Thus, in the near future, an auto-calibration tool associated with various optimal-algorithms will be mounted on the model to conduct sensitivity and uncertainty analysis. Furthermore, new simple modules to simulate various water qualities such as SS and TOC will be added to the model.

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References

1. United States Environmental Protection Agency (USEPA). *National Management Measures to Control Nonpoint Source Pollution from Agriculture*; EPA 841-B-03-004; U.S. Environmental Protection Agency Office of Water (4503T): Washington, DC, USA, 2003.
2. Holvoet, K.M.; Seuntjens, P.; Vanrolleghem, P.A. Monitoring and modeling pesticide fate in surface waters at the catchment scale. *Ecol. Model.* **2007**, *209*, 53–64. [[CrossRef](#)]

3. Jeon, J.H.; Yoon, C.G.; Donigan, A.S.; Jung, K.W. Development of the HSPF-Paddy model to estimate watershed pollutant loads in paddy farming regions. *Agric. Water Manag.* **2007**, *90*, 75–86. [[CrossRef](#)]
4. Li, Z.; Luo, C.; Xi, Q.; Li, H.; Pan, J.; Zhou, Q.; Xiong, Z. Assessment of the AnnAGNPS model in simulating runoff and nutrients in a typical small watershed in the Taihu Lake basin, China. *Catena* **2015**, *133*, 349–361. [[CrossRef](#)]
5. Ribarova, I.; Ninov, P.; Cooper, D. Modeling nutrient pollution during a first flood event using HSPF software: Iskar River case study, Bulgaria. *Ecol. Model.* **2008**, *211*, 241–246. [[CrossRef](#)]
6. Ryu, J.; Cho, J.; Kim, I.J.; Mun, Y.; Moon, J.P.; Kim, N.W.; Lim, K.J. Enhancement of SWAT-REMM to simulate reduction of total nitrogen with riparian buffer. *Trans. ASABE* **2011**, *54*, 1791–1798. [[CrossRef](#)]
7. Yang, G.; Best, E.P. Spatial optimization of watershed management practices for nitrogen load reduction using a modeling-optimization framework. *J. Environ. Manag.* **2015**, *161*, 252–260. [[CrossRef](#)] [[PubMed](#)]
8. Arnold, J.G.; Moriasi, D.N.; Gassman, P.W.; Abbaspour, K.C.; White, M.J.; Srinivasan, R.; Santhi, C.; Harmel, R.D.; van Griensven, A.; Van Liew, M.W.; et al. SWAT: Model use, calibration and validation. *Trans. ASABE* **2012**, *55*, 1491–1508. [[CrossRef](#)]
9. Bicknell, B.; Imhoff, J.; Kittle, J.; Jobs, T.; Donigan, A. *HSPF, User's Manual*; Version 12; U.S. Environmental Protection Agency: Athens, GA, USA, 2001; pp. 120–128.
10. Gironas, J.; Roesner, L.A.; Rossman, L.A.; Davis, J. A new applications manual for the Storm Water Management Model (SWMM). *Environ. Model. Softw.* **2010**, *25*, 813–814. [[CrossRef](#)]
11. U.S. Environmental Protection Agency (USEPA). *SWMM 5 User's Manual*; EPA/600/R-05/040; National Risk Management Research Laboratory, Office of research and Development: Cincinnati, OH, USA, 2010.
12. Edwards, C.; Miller, M. *PLOAD Version 3.0 User's Manual*; United States Environmental Protection Agency (USEPA): Washington, DC, USA, 2001.
13. Tetra Tech, Inc. *User's Guide Spreadsheet Tool for the Estimation of Pollutant Load (STEPL)*; Version 4.1; Tetra Tech, Inc.: Fairfax, VA, USA, 2011.
14. Park, Y.S.; Engel, B.A.; Harbor, J. A web-based model to estimate the impact of best management practices. *Water* **2014**, *6*, 455–471. [[CrossRef](#)]
15. Bhaduri, B.; Grove, M.; Lowry, C.; Harbor, J. Assessing the long-term hydrologic impact of land-use change: Cuppy McClure watershed, Indiana. *J. Am. Water Works Assoc.* **1997**, *89*, 94–106.
16. Engel, B.A. *GIS-based CN Runoff Estimation*; Agricultural and Biological Engineering Departmental Report; Purdue University: West Lafayette, IN, USA, 1997.
17. Harbor, J.M. A practical method for estimating the impact of land-use change on surface runoff, groundwater recharge and wetland hydrology. *J. Am. Plan. Assoc.* **1994**, *60*, 95–108. [[CrossRef](#)]
18. Lim, K.J.; Engel, B.A.; Tang, Z.; Muthukrishnan, S.; Choi, J.; Kim, K. Effects of calibration on L-THIA GIS runoff and pollutant estimation. *J. Environ. Manag.* **2006**, *78*, 35–43. [[CrossRef](#)] [[PubMed](#)]
19. Jang, C.H.; Kum, D.H.; Jung, Y.; Kim, K.; Shin, D.S.; Engel, B.A.; Shin, Y.; Lim, K.J. Development of a Web-based L-THIA 2012 direct runoff and pollutant Auto-calibration module using a genetic algorithm. *Water* **2013**, *5*, 1952–1963. [[CrossRef](#)]
20. Lim, K.J.; Engel, B.A.; Bhaduri, B.; Harbor, J. Development of the Long Term Hydrologic Impact Assessment Tool (L-THIA) WWW System. In Proceedings of the 10th International Soil and Conservation Organization Meeting, West Lafayette, IN, USA, 24–29 May 1999; pp. 1018–1023.
21. Ryu, J.; Kim, E.J.; Han, M.D.; Kim, Y.S.; Kum, D.H.; Lim, K.J.; Park, B.K. Enhancement of Estimation Method on the Land T-P Pollutant Load in TMDLs Using L-THIA. *J. Korean Soc. Environ. Eng.* **2014**, *36*, 162–171. [[CrossRef](#)]
22. Jang, J.H.; Jung, K.W.; Yoon, C.G. Modification of SWAT model for simulation of organic matter in Korean watersheds. *Water Sci. Technol.* **2012**, *66*, 2355–2362. [[CrossRef](#)] [[PubMed](#)]
23. Tang, Z.; Engel, B.A.; Lim, K.J.; Pijanowski, B.C.; Harbor, J. Minimizing the Impact of urbanization on long term runoff. *J. Am. Water Resour. Assoc.* **2005**, *41*, 1347–1359. [[CrossRef](#)]
24. Ahiablame, L.M.; Engel, B.A.; Chaubey, I. Representation and evaluation of low impact development practices with L-THIA-LID: An example for site planning. *Environ. Pollut.* **2012**, *1*, 1–13. [[CrossRef](#)]
25. Hawkins, R.H. Asymptotic determination of runoff curve numbers from data. *J. Irrig. Drain. Eng.* **1993**, *119*, 334–345. [[CrossRef](#)]
26. Ryu, J.; Jung, Y.; Kong, D.S.; Park, B.K.; Kim, Y.S.; Engel, B.A.; Lim, K.J. Approach of Land Cover based Asymptotic Curve Number Regression Equation to Estimate Runoff. *J. Irrig. Drain. Eng.* **2016**. in press.

27. Ryu, J.; Jang, W.S.; Kim, J.; Choi, J.D.; Engel, B.A.; Lim, K.J. Development of Watershed-scale Long term Hydrologic Impact Assessment Model with Asymptotic Curve Number Regression Equation. *Water* **2016**, *8*, 153. [[CrossRef](#)]
28. Bhaduri, B.A. GIS-Based Model to Assess the Long-Term Impacts of Land Use Change on Hydrology and Nonpoint Source Pollution. Ph.D. Thesis, Purdue University, West Lafayette, IN, USA, 1998.
29. Choi, J.D. *Effect of Agricultural Activities Farm Environment of Groundwater Quality*; DAESAN Agriculture Foundation: Seoul, Korea, 1995; pp. 434–444.
30. Han River Watershed Management Committee (HRWMC). *Research on Long Term Monitoring for the Non-point Source Discharge in Han River Basin*; National Institute Environmental Research (NIER): Incheon, Korea, 2014.
31. Nakdong River Basin Management Committee (GRBMC). *A Monitoring and Management Scheme for the Non-Point Sources in Nakdong River Basin*; National Institute Environmental Research (NIER): Incheon, Korea, 2004.
32. Geum River Basin Management Committee (GRBMC). *A Monitoring and Management Scheme for the Non-Point Sources in Geum River Basin*; National Institute Environmental Research (NIER): Incheon, Korea, 2014.
33. Youngsan River Basin Management Committee (GRBMC). *A Monitoring and Management Scheme for the Non-Point Sources in Youngsan River Basin*; National Institute Environmental Research (NIER): Incheon, Korea, 2014.
34. National Institute Environmental Research (NIER). *Public Hearing of Nonpoint Source Pollution Unit Load Survey*; National Institute Environmental Research (NIER): Incheon, Korea, 2014.
35. Brown, L.C.; Barnwell, T.O. *The Enhanced Water Quality Models QUAL2E and QUAL2E-UNCAS Documentation and User Manual*; EPA/600/3-87/007; United States Environmental Protection Agency (USEPA): Athens, GA, USA, 1987.
36. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 16th ed.; American Public Health Association, Inc.: Washington, DC, USA, 1985.
37. Cluis, D.; Couture, P.; Begin, R.; Visser, S.A. Potential eutrophication assessment in rivers; relationship between produced and exported loads. *Swiss J. Hydrol.* **1988**, *50*, 166–181. [[CrossRef](#)]
38. Stefan, H.G.; Preud'Homme, E.B. Stream temperature estimation from air temperature. *J. Am. Water Resour. Assoc.* **1993**, *29*, 27–45. [[CrossRef](#)]
39. Glavan, M.; Milicic, V.; Pintar, M. Finding options to improve catchment water quality Lessons learned from historical land use situations in a Mediterranean catchment in Slovenia. *Ecol. Model.* **2013**, *261*, 58–73. [[CrossRef](#)]
40. Na, J.S. Effects of Non-Point Pollutant Sources Using QUAL2E Model. Master's Thesis, Chosoen University, Gwang-ju, Korea, 2015.
41. Nash, J.E.; Sutcliffe, J.V. River flow forecasting through conceptual models, Part I—A discussion of principles. *J. Hydrol.* **1970**, *10*, 282–290. [[CrossRef](#)]
42. Glavan, M.; White, S.M.; Holman, I.P. Water quality targets and maintenance of valued landscape character—Experience in the Axe catchment, UK. *J. Environ. Manag.* **2012**, *103*, 142–153. [[CrossRef](#)] [[PubMed](#)]
43. Wischmeier, W.H.; Smith, D.D. *Predicting Rainfall Erosion Losses: A Guide to Conservation Planning*; USDA Agricultural Handbook No. 537; U.S. Government Printing Office: Washington, DC, USA, 1978.
44. Moriasi, D.N.; Arnold, J.G.; VanLiew, M.W.; Bingner, R.L.; Hrmel, R.D.; Veith, T.L. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Trans. ASABE* **2007**, *50*, 885–900. [[CrossRef](#)]
45. Ramanarayanan, T.S.; Williams, J.R.; Dugas, W.A.; Hauck, L.M.; McFarland, A.M.S. Using APEX to Identify Alternative Practices for Animal Waste Management. In Proceedings of the American Society of Agricultural Engineers Annual International Meeting, Minneapolis, MN, USA, 10–14 August 1997.
46. Duda, P.B.; Hummel, P.R.; Donigian, A.S., Jr.; Imhoff, J.C. BASINS/HSPF: Model use, calibration, and validation. *Trans. ASABE* **2012**, *55*, 1523–1547. [[CrossRef](#)]

