



## Applicability study of ecological impact assessment using AQUATOX model in Paldang Reservoir, South Korea

Chun Gyeong Yoon<sup>a</sup>, Han-Pil Rhee<sup>a,b,\*</sup>, Yeongkwon Son<sup>b,c</sup>

<sup>a</sup>Department of Environmental Health Science, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul, Korea, Tel./Fax: +82 (2) 450-3747; email: chunyoona@konkuk.ac.kr

<sup>b</sup>ET Waters Co. Ltd., 6 Neungdong-ro 16-gil, Gwangjin-gu, Seoul, Korea, Tel./Fax: +82 (2) 455-3931; email: hprhee@etwaters.co.kr

<sup>c</sup>Department of Environmental & Occupational Health Science, School of Public Health, Rutgers University, 683 Hoes Lane West, Piscataway, NJ, USA, Tel./Fax: +1 (732) 235-4889; email: sonye@sph.rutgers.edu

Received 23 January 2016; Accepted 8 July 2016

---

### ABSTRACT

The purpose of this study was to evaluate the applicability of the AQUATOX model and to suggest a methodology for its practical use as an ecological toxicity model in Korea. Paldang reservoir was selected as the study area, and the BASINS/WinHSPF watershed model was used in conjunction with AQUATOX model to provide a linked simulation of the Paldang watershed. The AQUATOX model was run based on the simulation results of WinHSPF. AQUATOX was used to perform an analysis of the ecological state and characteristics of the Paldang reservoir and the ecological impact of toxicants; alachlor, paraquat, and copper sulfate. In the case of alachlor, which has been classified as a second-degree toxic material for fish, the biomass of minnow and bass declined considerably when the inflow concentration was above 100 µg/L. In the case of paraquat, the biomass of minnow and bass declined significantly when the inflow concentration was 10 µg/L. Biomass of daphnia and bluegill was significantly decreased due to the copper sulfate. The AQUATOX model could be considered to be applicable to water bodies in Korea and can be used with existing watershed models to determine the total maximum daily load (TMDL). Seasonal or monthly ecological monitoring data of common species should be provided to increase its feasibility.

*Keywords:* AQUATOX; HSPF; Ecological modeling; Ecological risk assessment; TMDL

---

### 1. Introduction

South Korea is a densely populated country with over 48 million people living in an area of less than 100,000 km<sup>2</sup>. Until the late 1980s, rapid industrialization was responsible for severe damage to South Korea's natural environment. However, since then, environmental conditions have been improving due to various restoration programs. The "Special Act on Watershed Management for Four Major Rivers" enacted in 1998, includes several programs that aim to improve, maintain, or restore the water quality in national

water systems [1]. These programs include discharge limits, permits for point sources, funding for wastewater treatment facilities, and the setting of a total maximum daily load (TMDL). From 2010, over 90.1% of the domestic wastewater generated nationally was collected and treated in public sewers [2].

Recently in Korea, public interest in the quality of life has increased alongside improvements in the standard of living and a rise in the national income. The social consciousness toward water resources and quality, which can have a direct influence on life, the environment, and essential human activities, is rapidly changing. Water resource management oriented toward rivers to secure an adequate water supply and prevent disasters had been a major concern until

---

\* Corresponding author.

the late part of the last century. Water-quality management has now become one of the most important social issues in Korea. Following several high-profile environmental accidents, including the contamination of the Nakdong River by phenol in 1991 and organic solvents in 1994, public awareness of water-quality management and the environment was enhanced by active public relation programs including public campaigns and educational programs by governmental and nongovernmental organizations (NGOs).

Since the late-2000s, nonpoint sources, aquatic life, ecosystems, and environmental toxicity have become key words incorporated into environmental policies. The current environmental policies in Korea have the stated aim of the “protection and restoration of a sustainable, healthy, and sound environment,” and new systems, including toxicological evaluation and the risk assessment of treated sewage, pollutant release and transfer registers (PRTR) and the evaluation of healthy aquatic life, have been established [3].

Various modeling techniques have been applied as useful tools for the development of water-quality management policies through the establishment of suitable pollution control measures in watersheds, prior environmental review, prediction of future water quality, and the development of TMDL. However, meeting the targets of recent policies is difficult using only currently available modeling techniques. Most existing models have generally focused on physico-chemical water-quality parameters, coliform, and chlorophyll *a* (chl-*a*). Therefore, the development of new integrated modeling techniques, which can predict the environmental fate of various pollutants and their effects on aquatic life, is required.

The AQUATOX model is a general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients, sediment, and toxic chemicals in aquatic ecosystems [4,5]. This model can be applied through a link with the Better Assessment Science Integrating point and Nonpoint Sources (BASINS), Hydrologic Simulation Program-Fortran (WinHSPF), and the Soil and Water Assessment Tool (SWAT), which have already been used in the national water-quality modeling system in Korea [9]. In terms of policy direction and the social requirements for the water environment, AQUATOX is likely to be a very useful model in Korea. However, a full review of its applicability is essential for the introduction of this new modeling system, even though it has already been sufficiently verified in other countries [5–8]. Furthermore, AQUATOX is not yet commonly used, and the form of the data required is different from general ecological monitoring data.

To address these concerns, a study of the applicability of AQUATOX was performed and the methodology adopted for its practical use was reviewed. For this reason, the BASINS/WinHSPF model was used to produce a simulation for the Paldang watershed, and the AQUATOX model was then run based on the HSPF simulation results through the BASINS AQUATOX extension. Various ecological data were collected following a literature review and assessed the ecological impact due to inflows of selected toxicants (i.e., alachlor, paraquat dichloride and copper sulfate). The usefulness of AQUATOX was examined based on the stability and predictability of the model result.

## 2. Materials and methods

### 2.1. Study area

Paldang reservoir, which was selected as the study area, is the major source of water supply to Seoul metropolitan city and the capital area; Kyeongan stream and the North and South Han rivers flow into the reservoir. Cheongpyeong dam is located on the northeast side of the reservoir, and Ipo weir is located on the southeast shore (Fig. 1). Paldang reservoir is a riverine-type reservoir, with a relatively small surface area (36.5 km<sup>2</sup>) and storage capacity (244 million tons), average water depth (6.5 m), and short detention time (about 5.4 d) in comparison with the watershed area (23,800 km<sup>2</sup>) and average inflow rate (44 million tons/day). Paldang watershed includes parts of Gangwon-do, Gyeonggi-do, and Chungcheongbuk-do provinces. Thirty-three watersheds for TMDL and 13 large dams, including Paldang dam, are located in this watershed. The average annual precipitation is about 1,270 mm, approximately 70% of which falls in summer from July to September, with the remainder occurring from October to May. Due to the Asian monsoon cycle, precipitation has large seasonal and spatial variation [10].

### 2.2. Watershed modeling

The HSPF model (version 12.0) is a sophisticated continuous watershed model capable of simulating a hydrologic time series of runoff quantity–quality events [11]. It can be used to determine flows (hydrographs) and conventional pollutants (pollution graphs). HSPF has been widely used for watershed management because it is capable of simulating various hydrologic conditions [12,13], the transport of nonpoint source pollution, including contaminated sediment [14,15], and land-use management and flood control scenarios [16,17]. It also has been used to simulate water flow and water quality for water resource management in Korea [18–21].

In this study, the HSPF model was used as a preprocessor for AQUATOX to produce a linked simulation. Hourly precipitation, air temperature, dew point temperature, wind speed, cloud cover, and solar radiation were obtained from the 19 weather stations [22]. In total of 86 environmental-infrastructure facilities which had higher than 500 ton/day capacity was included as point source data [23]. Land-use map and digital elevation model (DEM) in the study area were obtained from the Korean Ministry of Environment [24]. Total of 23 land-use types from the original map was reclassified into seven categories of urban area, agricultural land, forest, pasture, wetland, barren land, and water. Sub-basins were determined by natural drainage boundaries using the DEM and the Paldang watershed was divided into 50 sub-basins.

### 2.3. Calibration and validation of watershed model

The calibration and validation for hydrologic simulations using the HSPF model were performed at the locations of the 31 TMDL monitoring stations, and water quality was assessed at 9 of these stations (Fig. 1) using observed data for Korean TMDL at 8-d intervals [23]. INFILT, KVARV and AGWRC, among the many parameters related to hydrologic

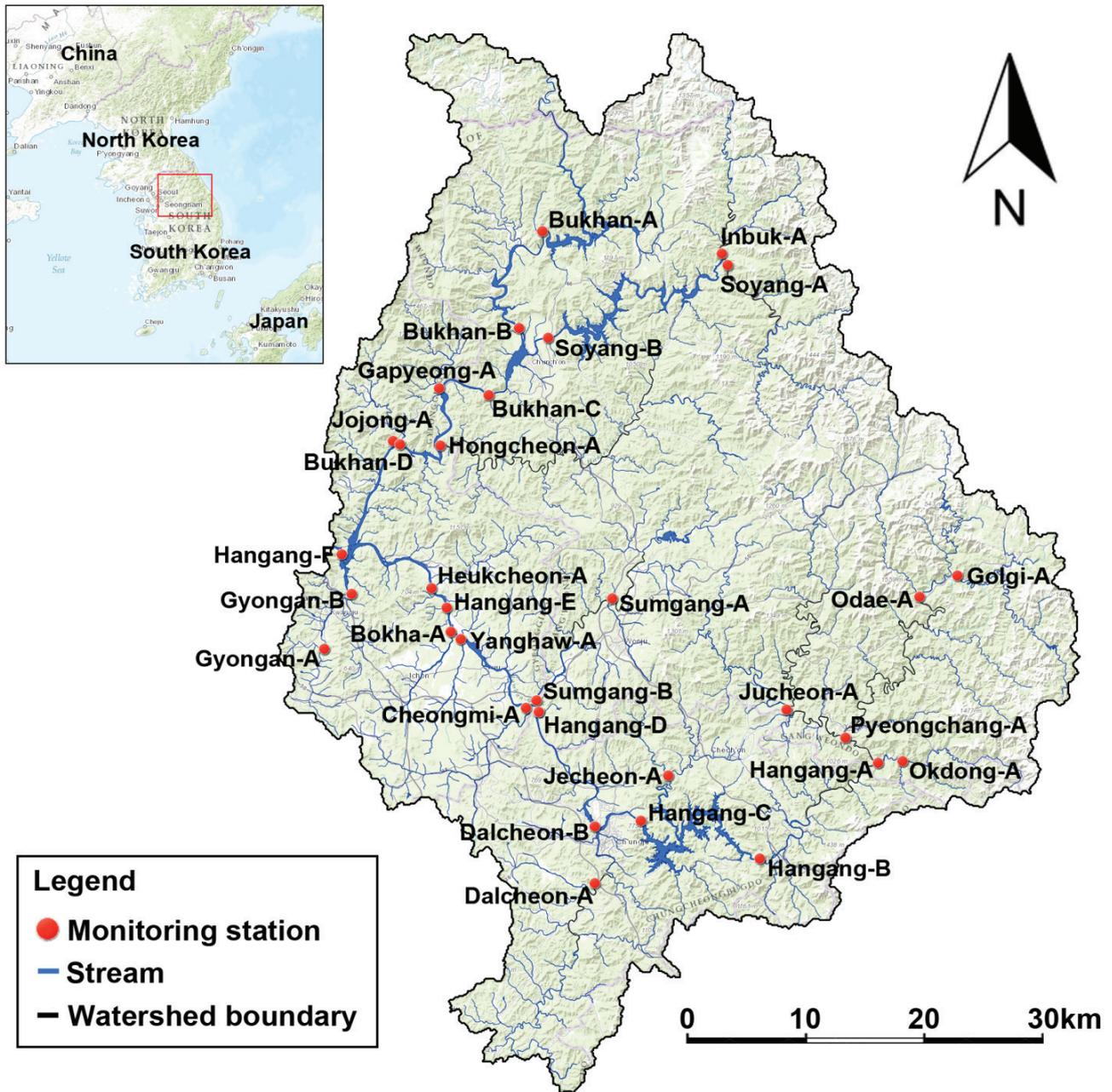


Fig. 1. Paldang reservoir watershed and location of monitoring stations.

simulation, were relatively sensitive. Calibration and validation for the water quality simulation, including water temperature, dissolved oxygen (DO), biochemical oxygen demand (BOD), total nitrogen (T-N), and total phosphorus (T-P), was performed for nine selected locations (Golgi-A, Hangang-B, Hangang-D, Hangang-E, Heukcheon-A, Bukhan-D, Jojong-A, and Kyongan-B) (Fig. 1). The period of calibration (2007–2008) and validation (2009–2010) was a total of 4 years, and the Nash-Sutcliffe efficiency (NSE) and RMSE-observations standard deviation ratio (RSR) was used to evaluate the model performance [25].

NSE measures normalized relationship between the residual and observed data variances [26]. NSE represents not only the correlation between observed and simulated value but also indicates how close the slope of regression line to 1. Optimal value of NSE is 1 and the model has “satisfactory” and “very good” if NSE value greater than 0.5 and 0.75, respectively [25]. RSR standardizes RMSE using standard deviation of observations. Zero residual variations or RMSE gives the optimal value of 0 for RSR. Less than or equal to 0.5 of RSR value indicates “very good” model performance and model performance is “satisfactory” when RSR is less than or equal to 0.7 [25].

#### 2.4. Application of AQUATOX

Data from HSPF were linked to the AQUATOX model through the BASINS AQUATOX extension. AQUATOX accepts inputs for the volume of water in the system, a time-series of nutrient loadings, a time-series of organic chemical loadings, and the physical characteristics of the system [27]. The AQUATOX model was applied to the Paldang reservoir based on the HSPF simulation results (geographic, meteorologic, hydrologic, and water-quality data) between 2007 and 2010. AQUATOX model was stabilized in 2007, and then the simulation results during 2008–2010 were used in this study. The linkage function of BASINS can support this process by converting data from the HSPF simulation results to an appropriate form, which compensates for the relatively vulnerable hydrologic simulation of AQUATOX.

The food web used in AQUATOX has to consist of at least one aquatic life-form for each trophic level. These life-forms are categorized as “Plants (algae and macrophytes),” “Invertebrates,” or “Fish” [27]. The plants category can be reclassified as diatoms, green algae, blue-green algae, other algae, and macrophytes. The second trophic level is zooplanktons. The invertebrate category includes shredders, bottom sediment feeders, suspended sediment feeders, clams, grazers, snails, and predatory invertebrates. Foraging fish, bottom fish, and game fish are sub-class of the fish category. All of the ecological data regarding aquatic life must be reclassified to the family or order level of biological classification and input as biomass (AFDM; mg/L

dry, g/m<sup>2</sup> dry). Finally, the information regarding trophic interactions among aquatic organisms was applied based on default values provided in AQUATOX as listed in Table 1 [27].

Algae and fish species included in this study were selected based on the data availability and model capability (Table 1). Ecological data (density: cells/L or ind./L and carbon content: µg C/L) regarding the plants and invertebrates of Paldang reservoir were collected through a literature review [9,28–31]. Carbon content (µg C/L) of algae and macrophyte is approximately 36% of its dry weight (mg/L dry) [32–35]. Pace et al. [36] considered the carbon content of zooplankton to be about 48% of dry weight. Therefore, biomass data as the dry weight of plants and zooplankton categories were obtained from the carbon content by applying a conversion factor (plants: 0.36 and zooplankton: 0.48). Five phytoplankton, including diatoms, green algae, blue-green algae, flagellates, and myriophyllum, and three zooplankton, including copepods, cladocerans, and rotifers, were selected to simulate algae population in this study [28]. The fish population and the dry weight of different species in the Han River system were obtained from NIER [30]. The four fish species, that is, minnow, bluegill, carp, and bass, were selected for model simulation because they had higher biomass compared with other species observed in Paldang reservoir and the AQUATOX has complete ecological database for the four species.

The population of zooplankton and phytoplankton were affected by not only the environmental conditions of

Table 1  
Initial condition (biomass) and trophic interactions among selected aquatic organisms in AQUATOX

Category			Initial biomass <sup>a</sup>	Trophic interactions (preference, %) [27]						
				Copepod	Cladoceran	Rotifer	Minnow	Bluegill	Carp	Bass
Refractory detritus of sediment			–							
Labile detritus of sediment			–					22.2		
Refractory detritus of particulate matter			–		13.0		8.2			
Labile detritus of particulate matter			–	9.1	43.5	10.0	8.2		22.2	
Plants	Phytoplankton	Diatom	0.553				18.4			
		Greens	0.481				18.4		5.6	
		Blue-Greens	0.036	54.5			18.4		5.6	
		Flagellate	0.380	36.4	43.5	90.0				
		Macrophyte	Myriophyllum	0.003						22.2
Invertebrates	Susp. Feeders <sup>b</sup>	Copepods	0.017				14.3	100.0	11.1	1.5
		Cladocerans	0.069				14.3		11.1	
		Rotifers	0.011							
Fish	Small forage	Minnow	3.131							10.6
	Large forage	Bluegill	2.253							7.3
	Large bottom	Carp	0.583							14.7
	Large game	Largemouth Bass	0.301							

<sup>a</sup>Phytoplankton and invertebrates is in the unit of mg/L dry and macrophyte and fish is in the unit of g/m<sup>2</sup> dry.

<sup>b</sup>Suspended sediment feeders.

the water body and its food supply but also by the inflow or outflow, because of their planktonic movement characteristics. In contrast, fish display a strong capacity for free movement and have relatively large body sizes compared with other aquatic organisms, allowing them to swim upstream. However, the movement of fish into Paldang reservoir is blocked by the Cheongpyeong dam in the direction of the North Han River and Ipo weir, which was started to build in 2009, in the direction of the South Han River. The movement or external loads of fish species were assumed to below 3% (the limit of the cross-sectional area of the water body at the reservoir boundary) of the internal population in this study to reflect current situation for the toxicant scenarios.

### 2.5. Scenarios

Alachlor, paraquat dichloride (paraquat), and copper sulfate were selected for use in the simulation of ecological impact in the AQUATOX model. Default chemical parameterization from the AQUATOX database was applied for the three chemicals. The acute toxicity data were obtained from literature review [37–39] and used in AQUATOX simulation (Table 2). Alachlor is one of the most popular herbicides and it has been detected several times in environmental samples in a range from 0.002 to 0.030  $\mu\text{g/L}$  [3]. Alachlor can produce adverse human health effects, including endocrine disruption, and damage to the eyes, liver, kidney, and spleen. Paraquat is also known as methyl viologen or Gramoxone and it has been very commonly used in agricultural practices in Korea [3]. Copper sulfate has been used as an additive in most livestock feeds in Korea [3]. The gain rate of livestock is improved when copper sulfate is mixed at a rate of 125–250 mg/kg in the feedstuff of pigs or chicken. Therefore, copper sulfate can be discharged into a water body alongside livestock manure [3,9]. Some aquatic organisms (copepods, minnows, carp, and bass) were excluded in the copper sulfate scenario due to a lack of toxicity data.

Hypothetical scenarios for model application were produced when the inflow concentration of each toxicant was increased exponentially to five levels [0 (control), 1, 10, 100,

and 1,000 ppb]. This scenario is impractical, but examining extreme changes in the biomass of aquatic organisms can be advantageous during relatively short model run times. The scenarios were applied to test whether the ecological effects and responses by aquatic organisms to the toxicants were reasonable because the aim of this study was to evaluate the applicability and availability of AQUATOX. Difference of 3 years average aquatic species biomasses between different toxicant scenarios (2008–2010) were tested using t-test in R 3.2.3 [40].

## 3. Results and discussions

### 3.1. HSPF model results

Calibrated model parameters were presented in Table 3 and the final values were selected to achieve highest NSE and lowest RSR. The specificity of the hydrologic simulation results became comparatively small because of the large area of each sub-basin considered in this study. Therefore, the adjustment of only three parameters (INFILT, KVARY, and AGWRC) was sufficient to achieve an acceptable level of hydrologic calibration results. The main parameters used for water quality calibration are KBOD20, KODSET, REAK, BRBOD and BRNIT. Generally, ELEV (elevation parameter) and LEVAP (parameter for the latent heat of vaporization) were the important parameters for the calibration of water temperature [19]. However, they were not used in this study because their use was considered unnecessary. The hydrologic simulation results were evaluated to be “Very good” for 28 sub-basins and “satisfactory” for 5 sub-basins based on the NSE and RSR values. Model performance for the water quality simulation showed “satisfactory” to “very good” level. The NSE and RSR values were summarized in Table 4.

### 3.2. Modeling results of AQUATOX

The monthly average biomass of algae, zooplankton and fish was presented in Fig. 2. Diatom and green algae showed highest population in September and flagellate increased in

Table 2  
Acute toxicity data for the three toxicants used in AQUATOX [37–39]

Aquatic life	Exposure time (hour)	Endpoint	Alachlor ( $\mu\text{g/L}$ )	Paraquat ( $\mu\text{g/L}$ )	Copper sulfate ( $\mu\text{g/L}$ )
Diatom	96	EC50	460	559	35
Green algae	96	EC50	460	0.55	5
Blue-green algae	96	EC50	4,600	1,120	85
Flagellates	96	EC50	460	559	35
Macrophyte	96	EC50	198	51	–
Copepod	48	LC50	35,003	11,680	–
Cladoceran	48	LC50	9,000	4,000	182
Rotifer	48	LC50	–	–	76
Minnow	96	LC50	5,000	41,090	–
Bluegill	96	LC50	2,800	13,000	1,500
Carp	96	LC50	3,311	15,000	–
Bass	96	LC50	2,891	20,045	–

Table 3  
The range of parameters used for hydrologic and water-quality calibration in HSPF

Parameter	Definition	Unit	Model range	Initial value	Final value
INFILT	Index to infiltration capacity	in./h	0.0001–100	0.16	0.1–0.27
KVARY	Variable groundwater recession	1/in.	0.0–5.0	0.0	0.0–0.8
AGWRC	Base groundwater recession	none	0.001–0.999	0.98	0.92–0.98
KBOD20	Unit BOD decay rate at 20°C	1/h	1.0E-30 ≤	0.004	0.004–0.067
KODSET	BOD settling rate	ft/h	0 ≤	0.027	0.011–0.027
REAK	Empirical constant in the equation used to calculate the reaeration coefficient	1/h	1.0E-30 ≤	0.2	0.05–0.2
BRBOD	Base release rate of BOD materials	mg/m <sup>2</sup>	0.0001 ≤	0.001	0.001–150
BRNIT	The benthal release rates of ammonia under aerobic and anaerobic condition	mg/m <sup>2</sup>	0.0 ≤	0.0	0.0–95

Table 4  
Range of the model performance parameter and evaluation result for HSPF simulation<sup>a</sup>

Parameter	Calibration (2007–2008)			Validation (2009–2010)				
	NSE <sup>b</sup>	RSR <sup>c</sup>		NSE <sup>b</sup>	RSR <sup>c</sup>			
Flow rate	0.678–0.958	S-VG	0.205–0.506	S-VG	0.768–0.966	VG	0.185–0.485	VG
Temperature	0.804–0.963	VG	0.193–0.568	S-VG	0.814–0.969	VG	0.176–0.432	VG
DO	0.654–0.802	S-VG	0.342–0.615	S-VG	0.765–0.801	VG	0.446–0.639	S-VG
BOD	0.503–0.953	S-VG	0.216–0.645	S-VG	0.559–0.737	S-VG	0.382–0.513	S-VG
T-N	0.624–0.923	S-VG	0.278–0.639	S-VG	0.685–0.945	S-VG	0.235–0.528	S-VG
T-P	0.579–0.809	S-VG	0.437–0.674	S-VG	0.512–0.884	S-VG	0.298–0.694	S-VG

<sup>a</sup>S and VG represents “satisfactory” and “very good” performance, respectively.

<sup>b</sup>Nash-Sutcliffe efficiency.

<sup>c</sup>RMSE-observations standard deviation ratio.

spring season. Zooplankton increased from early spring to summer. There were limited temporal biological monitoring data, but one study reported high pelagic zooplankton dry-weights between May and July 2008 in Paldang reservoir [41]. Peak zooplankton dry-weight was reported in May 2008 due to the high *B. longirostris* population of 0.546 mg DW/L [41]. Planktonic biomass was affected by climate, nutrient inflows, and hydrologic variation. However, the food web was also a very important factor in biomass variation, especially the biomass of zooplankton (copepods, cladocerans, and rotifers), which were commonly feeding on flagellates (36.4%–90.0% of preference) or blue greens (54.5% of preference by copepod) and were therefore related to the biomass of flagellates or blue greens, and not diatoms or green algae according to the AQUATOX database (Table 1). The biomass of minnows, which prefer algae and zooplankton, increased until autumn. Increased minnow population was related with decreased zooplankton. The biomass of carp, which is consumed by bass as a pray (14.7% of preference), decreased as the biomass of bass increased. Previous study surveyed fish population at the upstream of Paldang reservoir (i.e., Gyeongan stream) in June and October 2010, and the result showed that higher minnow and carp population was observed in June than in October 2010 [42]. The variation of the biomass of bass might be also related to that of minnows. Current AQUATOX model result showed that biomass of largemouth bass was increased from late summer and peak was observed

in October. Similarly, one study reported that total number of bluegill and largemouth bass was 2 and 6 in June 2010 and 207 and 20 in October 2010 using casting net method at the upstream of Paldang reservoir [42]. Further monitoring campaign needs to be considered because the survey method and location may change the observed fish species and population. Modeling the food web is considered to be very complex, but it can provide comprehensive information.

### 3.3. Application of scenarios

The AQUATOX simulation was used to examine the ecological impact of various scenarios, especially the variation in average biomass according to the inflow concentration of toxicants. Toxicant scenarios were simulated during a 3-year (2008–2010) period after stabilizing AQUATOX using initial year (2007). Average biomass for each scenario was tabulated in Table 5 and control scenario represents normal aquatic environment without any toxicant release.

Alachlor pollution scenario showed that the planktonic biomass did not vary significantly ( $p < 0.01$ ). Positive association was observed between Alachlor concentration and algae, zooplankton and Daphnia biomass. Diatom, green algae, flagellates and daphnia biomass was 0.150, 0.162, 0.167 and 0.047 mg/L in control scenario, respectively, and it was increased or similar for 1,000 µg/L of alachlor contamination due to the decline of predator populations as

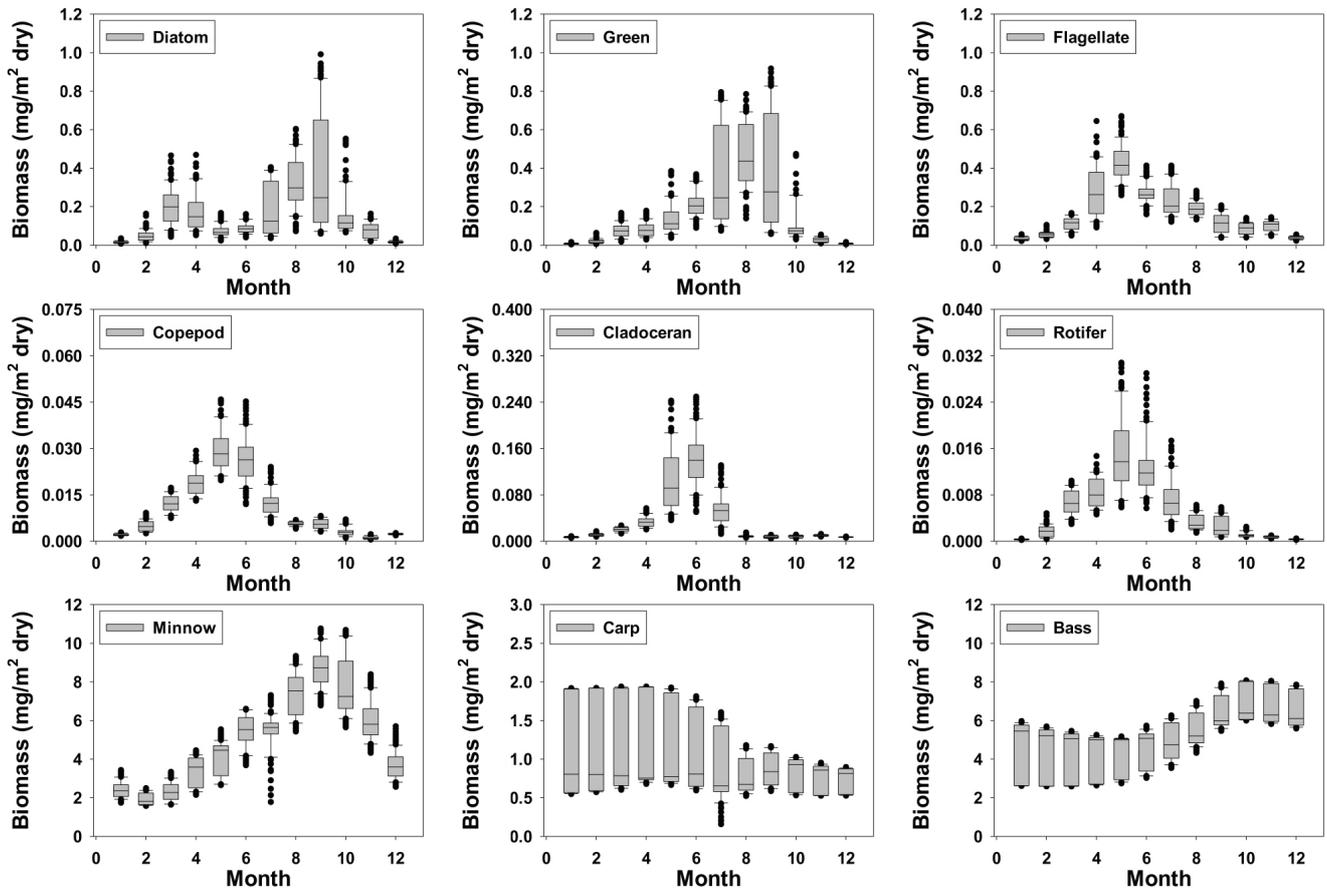


Fig. 2. Boxplot of monthly average biomass for each simulated aquatic species over a simulation period of 3 years.

Table 5  
Simulated average biomass according to the type and concentration of the toxicant scenario

Species	3 years average biomass according to the toxicant scenario														
	Alachlor (µg/L)					Paraquat (µg/L)					Copper sulfate (µg/L)				
	Control	1	10	100	1,000	Control	1	10	100	1,000	Control	1	10	100	1,000
Diatom (mg/L dry)	0.150	0.148	0.149	0.166	0.175	0.150	0.150	0.155	0.170	0.174	0.174	0.173	0.172	0.170	0.155
Green algae (mg/L dry)	0.162	0.161	0.161	0.181	0.190	0.162	0.162	0.168	0.185	0.189	0.194	0.189	0.187	0.188	0.182
Flagellates (mg/L dry)	0.167	0.164	0.164	0.164	0.164	0.167	0.167	0.164	0.163	0.164	0.199	0.163	0.162	0.164	0.153
Daphnia (mg/L dry)	0.047	0.047	0.047	0.060	0.070	0.047	0.047	0.051	0.066	0.069	0.070	0.070	0.068	0.044	0.015
Minnow (g/m <sup>2</sup> dry) <sup>a</sup>	4.761	4.775	4.718	2.027	0.103	4.761	4.761	3.800	1.139	0.317	–	–	–	–	–
Bluegill (g/m <sup>2</sup> dry)	0.629	0.601	0.602	0.851	1.322	0.629	0.629	0.613	1.058	1.256	1.423	1.405	1.224	0.531	0.030
Carp (g/m <sup>2</sup> dry) <sup>a</sup>	0.932	0.896	0.897	1.152	0.243	0.932	0.932	0.909	1.373	1.509	–	–	–	–	–
Largemouth Bass (g/m <sup>2</sup> dry) <sup>a</sup>	4.486	4.825	4.782	1.849	0.047	4.486	4.486	4.234	1.033	0.252	–	–	–	–	–

<sup>a</sup>Minnow, carp and largemouth bass was not included in the AQUATOX model for the copper sulfate due to the lack of toxicity information.

described below. These floating communities could continuously enter into the reservoir from upstream during the period of the simulation. In addition, death rate was low due to the  $EC_{50}$  of the plant category was established to be from 460 to 4,600  $\mu\text{g/L}$  ( $LC_{50}$ : 14,290–142,900  $\mu\text{g/L}$ , Table 2), which was higher than the inflow concentration in the various scenarios. However, the biomass of fish, including minnow, carp and bass, displayed significant decrease in the higher level of alachlor contamination ( $p < 0.05$ ). Minnow and largemouth bass was dominant species in control scenario, but biomass of minnow and largemouth bass was decreased to 0.103  $\text{g/m}^2$  (98% decrease) and 0.047  $\text{g/m}^2$  (99% decrease), respectively. Decreased predator population (i.e., minnow or largemouth bass) might effect on biomass of small species located in lower food chain (i.e., algae or bluegill).

In the case of paraquat scenario, the planktonic biomass displayed similar results to those observed for alachlor ( $p < 0.01$ ). Biomass of diatom, green algae, flagellates and daphnia was 0.174, 0.189, 0.164 and 0.0169 for 1,000  $\mu\text{g/L}$  of paraquat scenario, respectively. The  $LC_{50}$  (4,000–41,090  $\mu\text{g/L}$ ) and  $EC_{50}$  (0.55–1,120  $\mu\text{g/L}$ ) for paraquat were lower than those for alachlor (Table 2), but higher elimination rate constant and decreased predation might give similar survival rate for algae population. Algae and zooplankton have a relatively higher elimination rate constant (11,252–391,085) for paraquat than alachlor [43]. Minnow and largemouth bass was most sensitive species among the tested aquatic life. The biomass of minnows and largemouth bass decreased significantly depending on the paraquat concentration ( $p < 0.01$ ), but we observed opposite relationship for bluegill and carp. Bluegill has the highest elimination rate constant for alachlor and paraquat among these fish species (about 18 times that of largemouth bass) [37,39]. Furthermore, it has a relatively low lipid fraction which can store pesticides [37].

Control scenario results for the copper sulfate were different compared with the alachlor and paraquat because minnow, carp and largemouth bass was excluded in the AQUATOX simulation. The simulation results for the copper sulfate scenario indicated that there was no difference in algae population ( $p < 0.05$ ). Copper sulfate is well-known algacide, but the impact was not observed due to the inflow algae biomass. The biomass of daphnia decreased from 0.070  $\text{mg/L}$  to 0.015  $\text{mg/L}$  for 1,000  $\mu\text{g/L}$  of copper sulfate scenario (79% decrease), although both a decrease in predators and a continuous inflow of zooplankton from upstream occurred. The biomass of bluegill also decreased when concentrations were above 10  $\mu\text{g/L}$  and significantly lower biomass was observed (up to 98% decrease) at concentrations above 100  $\mu\text{g/L}$  ( $P < 0.01$ ).

### 3.4. Strengths and limitations

This study successfully explored feasibility of the HSPF-AQUATOX simulation applicable to water bodies in Korea and can be used in conjunction with other established watershed and water-quality models for Korean TMDL practices. The AQUATOX model could generate stable results without crashing or exploding. The result from three scenarios might provide better understanding of the impact of chemical compounds. However, following limitations should be addressed to make the AQUATOX applicable in Korea.

The limitation of this study is that the AQUATOX model could not be calibrated due to the lack of ecological monitoring data. In order to guarantee the reliability of prediction, site-specific calibration should be conducted depending on the objectives and data availability [5]. The detailed ecological monitoring data and information for various toxicants in a water body are essential to resolve data gap. The continuous seasonal monitoring of ecological data that expressed as dry biomass should adopt the biological classification of phytoplankton, periphyton, macrophytes, invertebrates (including zooplankton) and dominant fish species in the water body. Additional data of toxicants ( $\mu\text{g/L}$ ) in the water body and from chemical discharge facilities, including PRTR data, should be collected depending on the study goal. If the weaknesses related to hydraulics can be overcome by supplementing with other suitable models, such as EFDC, the AQUATOX will become more available for prediction and analysis in sustainable water resource management. Moreover, the AQUATOX database for the trophic interaction might not appropriate to the Korean aquatic environment. The trophic interactions were based on the foreign species, so it needs to be updated to reflect Korean domestic species. Database of average biomass, feeding behavior and chemical uptake rate for aquatic organisms can improve the applicability of the AQUATOX.

Despite of the limitations, the AQUATOX model has a relatively high compatibility with existing watershed models for TMDL, such as HSPF and SWAT. The AQUATOX can be applied to reflect the current conditions in Korea, where a social consensus regarding the importance of healthy ecosystems and toxicologically safe water resources has formed. The AQUATOX is expected to be usable as a scientific tool for safe and sustainable water resource management, if this model is properly used to predict ecological impacts and risk.

## 4. Conclusion

This study was initiated to evaluate the applicability of AQUATOX and to determine a methodology for its practical use as an ecological toxicity model in South Korea. The AQUATOX model was used in conjunction with BASINS/WinHSPF to produce a linked simulation. The AQUATOX model was used to predict ecological states and characteristics, including seasonal variation associated with trophic levels in the Paldang reservoir. The ecological impact of an inflow of toxicants was also assessed using hypothetical scenarios. The AQUATOX could address three scenarios but the significant data challenges (e.g., ecological observation and trophic interaction data) need to be resolved to apply AQUATOX in Korea. Therefore, further monitoring campaigns and pilot scale experiments will be conducted to calibrate AQUATOX model to be applied as an integrated modeling package for the Korean TMDL program.

## Acknowledgement

This paper was supported by Konkuk University in 2013.

## References

- [1] H.P. Rhee, C.G. Yoon, S.J. Lee, J.H. Choi, Y.K. Son, Analysis of nonpoint source pollution runoff from urban land uses in South Korea, *Environ. Eng. Res.*, 17 (2012) 47–56.

- [2] KME, 2013 Sewer Statistics, Korea Ministry of Environment, Seoul, South Korea, 2015 (in Korean).
- [3] KME, Investigation of Toxicants for Expansion of Management Target and Development of Control Measure, Korea Ministry of Environment, Seoul, South Korea, 2008 (in Korean).
- [4] U.S. EPA, Modeling Environmental Fate and Ecological Effects in Aquatic Ecosystems: Volume 2. Technical Documentation, Office of Water, U.S. Environmental Protection Agency, Washington D.C., 2009.
- [5] R.A. Park, J.S. Clough, M.C. Wellman, AQUATOX: modeling environmental fate and ecological effects in aquatic ecosystems, *Ecol. Model.*, 213 (2008) 1–15.
- [6] L. Bingli, S. Huang, Q. Min, L. Tianyun, W. Zijian, Prediction of the environmental fate and aquatic ecological impact of nitrobenzene in the Songhua River using the modified AQUATOX model, *J. Environ. Sci.*, 20 (2008) 769–777.
- [7] A. Akkoyunlu, Y. Karaaslan, Assessment of improvement scenario for water quality in Mogan Lake by using the AQUATOX Model, *Environ. Sci. Pol. Res.*, 22 (2015) 14349–14357.
- [8] A. Lombardo, A. Franco, A. Pivato, A. Barausse, Food web modeling of a river ecosystem for risk assessment of down-drain chemicals: a case study with AQUATOX, *Sci. Tot. Environ.*, 508 (2015) 214–227.
- [9] KME, Research on the Actual Condition of Provisional Managed Toxicants in the Hanriver Basin and Development of Prediction System, Korea Ministry of Environment, Seoul, South Korea, 2008.
- [10] S.B. Lee, C.G. Yoon, K.W. Jung, J.H. Jang, D.H. Rhew, Watershed-scale modeling to estimate delivery ratio of pollutant loads to support TMDL application in Korea, *Desal. Wat. Treat.*, 19 (2010) 64–73.
- [11] B.R. Bicknell, J.C. Imhoff, J. Kittle, T.H. Jobes, A. Donigian, HSPF Version 12 User's Manual, National Exposure Research Laboratory, Office of Research and Development US Environmental Protection Agency, 2001.
- [12] M. Albek, Ü.B. Ögütveren, E. Albek, Hydrological modeling of Seydi Suyu watershed (Turkey) with HSPF, *J. Hydrol.*, 285 (2004) 260–271.
- [13] P.J. Zarriello, K.G. Ries, A Precipitation-Runoff Model for Analysis of the Effects of Water Withdrawals on Streamflow, Ipswich River Basin, Massachusetts, U.S. Department of the Interior, U.S. Geological Survey, Milford, 2000.
- [14] A. Donigian, J. Love, Sediment calibration procedures and guidelines for watershed modeling, *P. Water Environ. Fed.*, 4 (2003) 728–747.
- [15] P.R. Hummel, J.L. Kittle, P.B. Duda, A. Patwardhan, Calibration of a watershed model for Metropolitan Atlanta, *P. Water Environ. Fed.*, 4 (2003) 781–807.
- [16] A. Donigian Jr., R. Chinnaswamy, T. Jobes, Conceptual Design of Multipurpose Detention Facilities for Flood Protection and Nonpoint Source Pollution Control, Aqua Terra Consultants, Mountain View, 1997, p. 151.
- [17] S. Brun, L. Band, Simulating runoff behavior in an urbanizing watershed, *Computers, Environ. Urban Sys.*, 24 (2000) 5–22.
- [18] S. Im, K. Brannan, S. Mostaghimi, J. Cho, A Comparison of SWAT and HSPF Models for Simulating Hydrologic and Water Quality Responses from an Urbanizing Watershed, ASAE Annual Int. Meeting, 2003.
- [19] H. Hwang, Applicability Study of BASINS/WinHSPF on TMDL in Korea, PhD Dissertation, Department of Rural Engineering, Konkuk University, Seoul, Korea, 2007 (in Korean).
- [20] J.H. Jeon, C.G. Yoon, A.S. Donigian, K.W. Jung, Development of the HSPF-Paddy model to estimate watershed pollutant loads in paddy farming regions, *Agr. Water Manage.*, 90 (2007) 75–86.
- [21] K.W. Jung, C.G. Yoon, J.H. Jang, H.C. Kim, Quantitative estimation of pollution loading from Hwaseong watershed using BASINS/HSPF, *J. Korean Soc. Agr. Eng.*, 49 (2007) 61–74 (in Korean).
- [22] KMA, Domestic Meteorological Data: Historical Data, Korean Meteorological Administration, Seoul, South Korea, 2015 (in Korean). Available at: <http://www.kma.go.kr>.
- [23] KME, National Pollution Survey Data, Korea Ministry of Environment, Seoul, South Korea, 2015 (in Korean). Available at: <http://wems.nier.go.kr>.
- [24] KME, Environmental Spatial Information Services, Korea Ministry of Environment, Seoul, South Korea, 2015 (in Korean). Available at: <http://egis.me.go.kr>.
- [25] D. Moriasi, J. Arnold, M. Van Liew, R. Bingner, R. Harmel, T. Veith, Model evaluation guidelines for systematic quantification of accuracy in watershed simulations, *Trans. ASABE*, 50 (2007) 885–900.
- [26] J. Nash, J.V. Sutcliffe, River flow forecasting through conceptual models. Part I: a discussion of principles, *J. Hydrol.*, 10 (1970) 282–290.
- [27] U.S. EPA, Modeling Environmental Fate and Ecological Effects in Aquatic Ecosystems: Volume 3. User's Manual for the BASINS Extension to AQUATOX Release 2.1, Office of Water, U.S. Environmental Protection Agency, Washington D.C., 2005.
- [28] S.H. Uhm, Study on the Grazing Relationship and Energy Transfer between Zooplankton and Phytoplankton and Bacteria in Lake Paldang Ecosystem, MS Thesis, Department of Rural Engineering, Konkuk University, Seoul, Korea, 2007 (in Korean).
- [29] NIER, Trophic Dynamics and Energy Flow of Plankton Food Web in Lake Paldang, National Institute of Environmental Research, Incheon, South Korea, 2005 (in Korean).
- [30] NIER, Survey on Environment and Ecosystem of Lakes in the Han River, National Institute of Environmental Research, Incheon, South Korea, 2006 (in Korean).
- [31] U.S. McKnight, S.G. Funder, J.J. Rasmussen, M. Finkel, P.J. Binning, P.L. Bjerg, An integrated model for assessing the risk of TCE groundwater contamination to human receptors and surface water ecosystems, *Ecol. Eng.*, 36 (2010) 1126–1137.
- [32] A.S. Rosemarin, Phosphorus nutrition of two potentially competing filamentous algae, *Cladophora glomerata* (L.) Kütz. and *Stigeoclonium tenue* (Agardh) Kütz. from Lake Ontario, *J. Great Lakes Res.*, 8 (1982) 66–72.
- [33] R.J. Stevenson, M.L. Bothwell, R.L. Lowe, J.H. Thorp, *Algal Ecology: Freshwater Benthic Ecosystem*, Academic Press, Cambridge, 1996.
- [34] L.A. Anderson, On the hydrogen and oxygen content of marine phytoplankton, *Deep-Sea Res. Pt. I*, 42 (1995) 1675–1680.
- [35] S.W. Bunting, J. Pretty, *Aquaculture Development and Global Carbon Budgets: Emissions, Sequestration and Management Options*, University of Essex, Colchester, UK, 2007.
- [36] M.L. Pace, J.D. Orcutt, The relative importance of protozoans, rotifers, and crustaceans in a freshwater zooplankton community, *Limnol. Oceanogr.*, 26 (1981) 822–830.
- [37] F.L. Mayer, M.R. Ellersieck, *Manual of Acute Toxicity: Interpretation and Data Base for 410 Chemicals and 66 Species of Freshwater Animals*, U.S. Department of the Interior, Fish and Wildlife Service, Washington D.C., 1986.
- [38] J. Fairchild, A. Allert, L. Sappington, B. Waddell, Chronic toxicity of un-ionized ammonia to early life-stages of endangered Colorado Pikeminnow (*Ptychocheilus lucius*) and Razorback Sucker (*Xyrauchen texanus*) compared to the surrogate Fathead Minnow (*Pimephales promelas*), *Arch. Environ. Con. Tox.*, 49 (2005) 378–384.
- [39] U.S. EPA. ECOTOX Database, U.S. Environmental Protection Agency, Washington D.C., 2015. Available at: <http://cfpub.epa.gov/ecotox/>.
- [40] R Development Core Team, *R: A Language and Environment for Statistical Computing*, Vienna, Austria, 2015.
- [41] J.S. Kang, S.B. Joo, S.J. Nam, G.R. Jeong, D.W. Yang, H.K. Park, S.K. Park, Secondary productivity of pelagic zooplankton in Lake Paldang and Lake Cheongpyeong, *J. Ecol. Field Biol.*, 32 (2009) 257–265.
- [42] E.H. Lee, M. Kim, H.M. Kim, M. Son, K.H. Chang, G.S. Nam, Ecological characteristics and distribution of fish in the downstream region of Gyeongan stream, *Korean Soc. Limnol.*, 31 (2013) 478–485 (in Korean).
- [43] J.F. Fairchild, L.C. Sappington, D.S. Ruessler, An Ecological Risk Assessment of the Potential for Herbicide Impacts on Primary Productivity of the Lower Missouri River, U.S. Department of the Interior, U.S. Geological Survey Toxic Substances Hydrology Program, Milford, 1999, pp. 323–330.