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Management of organic matter in watersheds with insufficient observation data: the Nakdong River basin

Jeonghoon Lee[a], Ungtae Kim[a], Lee-Hyung Kim[b], Eung Seok Kim[c], Sangdan Kim[d,*]

[a]*Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, OH 44115, USA*
[b]*Department of Civil and Environmental Engineering, Kongju National University, 1223-24, Cheonan-daero, Seobuk-gu, Cheonan, Chungcheongnam-do, 31080, Korea*
[c]*Division of Architecture Engineering and Civil Engineering, Sunmoon University, 70, Sunmoon-ro 221 beon-gil, Tangjeong-myeon, Asan, Chungcheongnam-do, 31460, Korea*
[d]*Department of Environmental Engineering, Pukyong National University, 45, Yongso-ro, Nam-gu, Busan, 48513, Korea, email: skim@pknu.ac.kr*

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ABSTRACT

Total organic carbon (TOC), which is represented as the total amount of organic matter in water, has emerged as a new water quality indicator. As TOC provides integrated information for managing water quality and sequential ecosystem of a watershed, sound scientific methods to analyze long-term spatiotemporal patterns of TOC have been sought recently. However, it is hard to find enough observed TOC data for watershed management. This study aims to develop a simple, yet reliable framework to analyze the TOC discharge from a complex and large watershed including many sub-basins and non-point sources. This study couples a daily streamflow model (revised TANK model) with two statistical water quality models (nutrition from watersheds and water treatment plants) to predict TOC at important control points in the Nakdong River basin in South Korea for demonstration. This methodology is expected to provide reasonable results even in watersheds with minimal observational data, since the spatial and temporal variation of TOC hydrologic fluxes can be examined by conceptualizing the watershed using discontinuous observation data.

Keywords: Hydrologic fluxes; Nakdong River; Total maximum daily loads; Total organic carbon

1. Introduction

Reduction and management of organic matter is crucial to control the water quality of receiving water bodies. To identify the spatial and temporal variability of emission of organic matter is the key step of establishing implementable water quality management policies in a watershed.

Biological oxygen demand (BOD) and chemical oxygen demand (COD) are indirect measures of organic matter in water. COD includes both biodegradable and non-biodegradable substances whereas BOD contains only bio-degradable. Those two parameters are most popular indicators of organic matter adopted in South Korea. However, recent studies revealed that BOD or COD as an indicator of organic matter has limitations to provide integrated information for water quality management [1]. BOD has limitations such as factors of error such as toxic substance, refractory substance, algae, nitrification, difficulty of analysis process and minimum analysis period of 5 d. Since COD can compensate for errors due to nitrification and algae, it can be a relatively accurate organic indicator compared with BOD. However, COD has pointed out various limitations due to large analysis error caused by pollutant properties. Therefore, the existing BOD and COD based

* Corresponding author.

water quality management do not properly reflect the total amount of pollutants and characteristics of organic matter [2]. Recently, total organic carbon (TOC) representing the total amount of organic matter in water has emerged as a new water quality indicator [3,4]. There are two most well-known methods to oxidize TOC in the analysis. They are the thermo-oxidation method, and the UV-persulfate oxidation. In the thermo-oxidation method, organic matter in water samples is thermally oxidized to CO_2 which is sequentially analyzed. In the UV-persulfate oxidation, organic matter in water samples is photo-oxidized in the presence of persulfate [5]. TOC is a more convenient and direct expression of total organic matter than BOD or COD. Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by BOD and COD [6].

The organic matters discharged from non-point pollutant sources show an increasing trend mainly due to urbanization and industrialization. In addition, shifts in rainfall patterns caused by climate change likely accelerate this trend [7]. As TOC provides integrated information for managing water quality and sequential ecosystem of a watershed, sound scientific methods to analyze long-term spatiotemporal patterns of TOC have been sought recently. TOC characteristics may include its sources, concentration distributions in time and space, bio-geochemical properties, and physiochemical behaviour in various water bodies.

For the purpose of best management practice in large complex watersheds, practical yet accurate mathematical models are required to consider heterogeneous soil types and land use under various management conditions over long periods of time. To effectively apply those mathematical models to decision making, conceptual or empirical parameters must be calibrated against the long-term observed data such as time series of streamflow and water quality.

The more the model is complex, the more observed data are required for calibration to reasonable result. In practice, however, it is hard to find enough observed data (especially TOC) for watershed management. This study aims to develop a simple, yet reliable framework to analyze the TOC discharge from a complex and large watershed including many sub-basins and non-point sources. This study couples a daily streamflow model (revised TANK model) with two statistical water quality models (nutrition from watersheds and water treatment plants) to predict TOC at important control points in the Nakdong River basin in South Korea for demonstration.

2. Methods

2.1. Study area

The Nakdong River basin is situated in the southeast of Korea between longitude 127°29′19″–129°18′00″ and latitude 34°59′41″–37°12′52″ (Fig. 1). The basin has a drainage area of about 23,690 km^2, it is 1/4 the size of Korea. According to the total maximum daily load (TMDL) management plan, the Nakdong River basin is divided into 41 sub-basins, the National Institute of Environmental Research (NIER) has conducted the survey on streamflow and water quality at the outlets of sub-basins every 8 d from August 2004. The target water quality parameters are pH, water temperature, electrical conductivity, DO, suspended solids (SSs), BOD_5, COD, total nitrogen, total phosphorus (TP) and TOC have been added since March 2007. The red hollow ovals indicate major wastewater treatment facilities that were notated as SS, GM, SC, DS and SB from north to south in Fig. 1. The red trapezoidal shape represents the location of the large dam, and AD, IH, HC and NG are abbreviations for each dam name (AnDong, ImHa, HapCheon and NamGang, respectively).

2.2. Data for hydrology and water quality

The revised TANK model adopted in this study uses daily precipitation, air temperature, relative humidity, wind speed, solar radiation, sunshine duration as inputs. Those input data were collected for 19 meteorological stations to cover the entire study area, which are available from Korea Meteorological Administration (www.kma.go.kr) since January 1988. Streamflow and water quality measurements were obtained from Water Information System (http://water.nier.go.kr) since August 2004 (in case of TOC, since March 2007).

Daily inflow and outflow hydrographs of four large dams (AD, IH, HC and NG dam) were collected from Water Resources Management Information System (www.wamis.go.kr) to consider the artificial effects of their flow controls. For sub-basins downstream of the dam, artificial flow control effect can be considered by using the collected daily inflow and outflow hydrographs as model inputs.

2.3. Watershed conceptualization

The study area was characterized as hydrologic components for streamflow simulation using a conceptual rainfall-runoff hydrologic model. This study utilizes the existing 41 sub-basins where TMDL is computed and 4 additional sub-basins (AnDong, ImHa, HapCheon and NamGang Dam) defined in this study to consider the effects of anthropogenic flow control by dams. Fig. 2 shows the details of the characterized study area.

This study proposes to couple a conceptual daily rainfall-runoff model (TANK) and statistical water quality models to estimate TOC at each sub-basin. First, the revised TANK model [8–11] in which river routing and evapotranspiration functions are incorporated to the conventional one is applied to simulate the long-term daily streamflow data. The parameters of the revised TANK model are calibrated to reproduce the 8 d interval observed streamflow data at the sub-basin outlet by NIER, Republic of Korea.

Second, the simulated streamflow data are used as input data for the seven-parameter log-linear model to simulate the long-term daily water quality (BOD, COD and TOC) loads. At this time, seven parameters are estimated using the minimum variance unbiased estimator to reproduce the 8 d interval observed water quality data.

Third, the regression analysis between BOD, COD and TOC effluent concentration data monitored from major wastewater treatment plants (WWTPs) is performed to

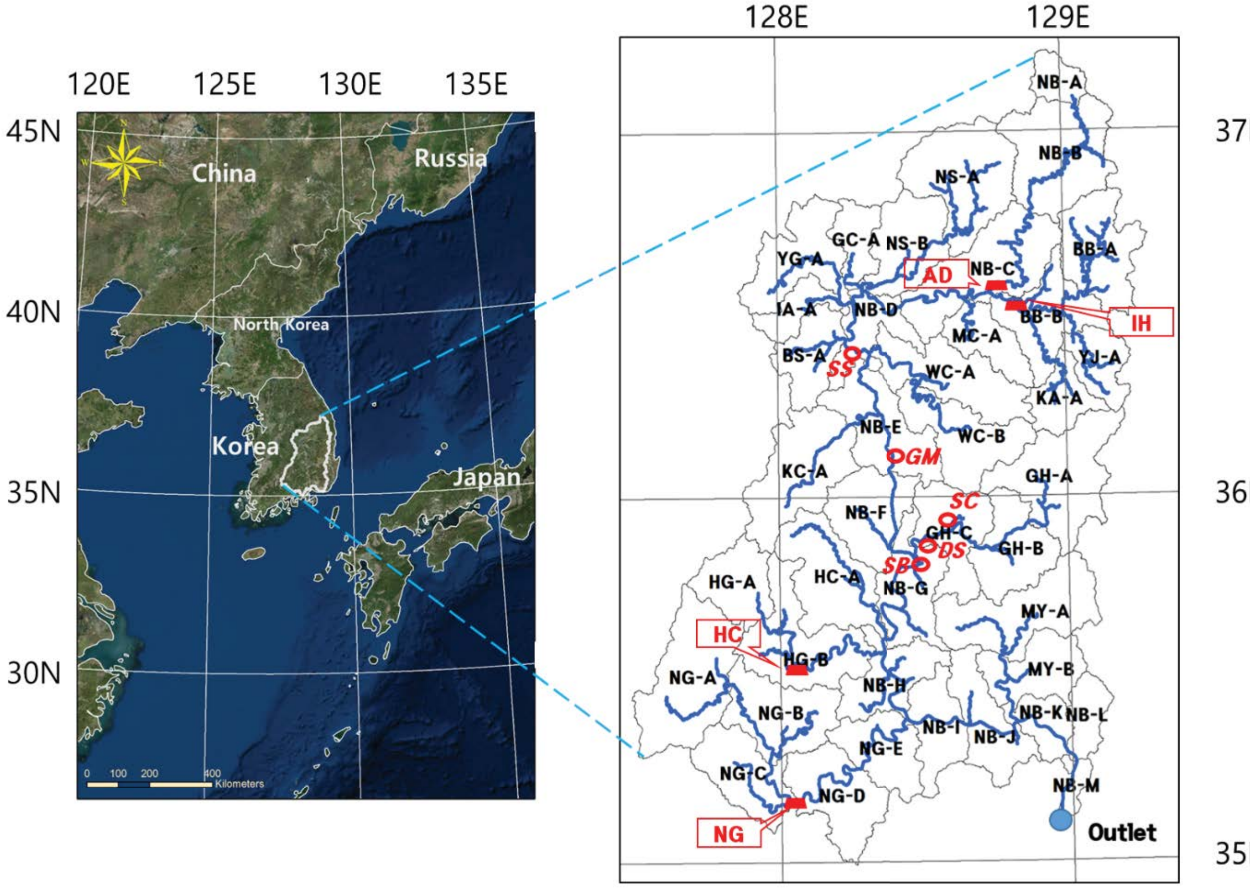


Fig. 1. Location of the Nakdong river basin and its sub-basins with river networks.

estimate TOC effluent concentration from all WWTPs. These TOC effluent concentrations can be used to calculate the contribution of point sources.

From the results of a series of analysis processes using available observed data, the contribution of point sources for TOC hydrologic fluxes will be quantified in the Nakdong River basin. Fig. 3 shows the schematic diagram for this study.

2.4. Daily stream flow simulation

The original TANK model [12] is a conceptual rainfall-runoff model based on accounting soil moisture in four layers of a tank while generating runoff through an orifice when soil moisture above a threshold level. Due to its capability in moisture accounting in long term simulation, the model has been widely applied to many water resources projects with various modifications. Studies by Kim and Kaluarachchi [13,14] suggested to use an adjusted potential evapotranspiration method calibrated to a target watershed for long-term simulation of water budget for Blue Nile River Basin. As a relevant domestic research, Kang et al. [15] conducted a study on calibration of TANK model with soil moisture structure and confirmed two types of objective functions for model calibration, Lee and Kang [16] in a study derived a multiple regression equation to estimate the regional parameters of the TANK model. However, most of the studies focus on calibration of the model and did not consider the channel routing. The original TANK models can be used when the watershed area is relatively small, but they are difficult to use when the watershed area is large as in the Nakdong River basin without considering the channel routing. Especially, the existence of a large dam makes it more difficult to apply because the hydrological characteristics of the upstream and downstream are completely different.

This study proposes to use the Muskingum hydrologic channel routing method [17], the most widely used for natural stream channel [18], to consider storage and transport effects in channels from upstream to downstream watersheds seamlessly rather than adding up their runoff hydrographs conventionally. This modification enables to simulate transport of TOC toward downstream sub-basins.

Fig. 4 demonstrates a schematic diagram that runoff hydrograph (Q_A) from sub-basin A is routed via a reach (dashed arrow) before combining with runoff hydrograph (Q_B) at sub-base B.

- Water stored in each TANK is spilled (right direction) or infiltrated (downward direction).
- Rainfall flows into the first tank (top), and initial loss such as surface storage, infiltration and evapotranspiration occur

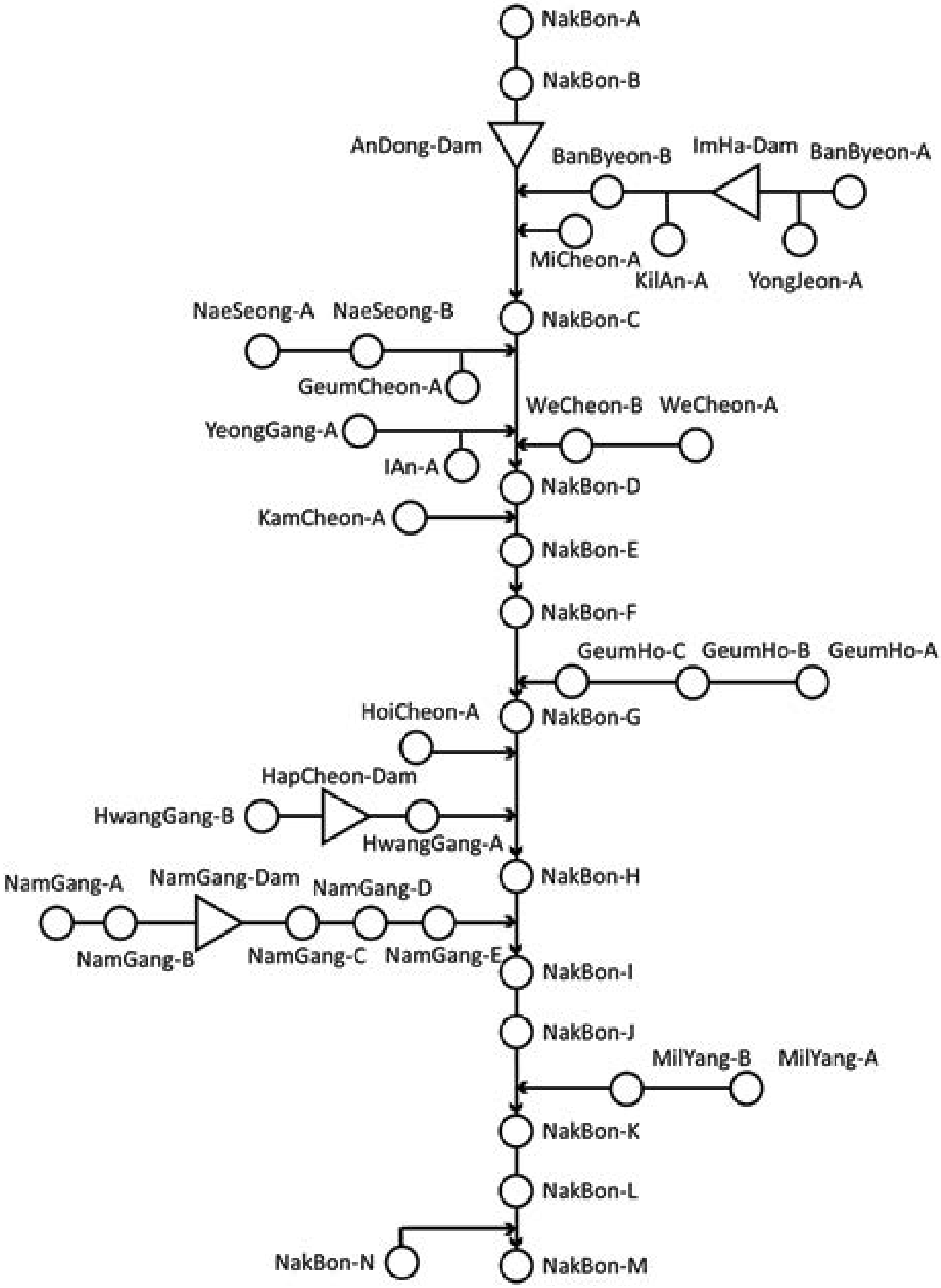


Fig. 2. Sub-basins (circle), large dams (triangle) and river networks (line) of the Nakdong River basin for the revised TANK model.

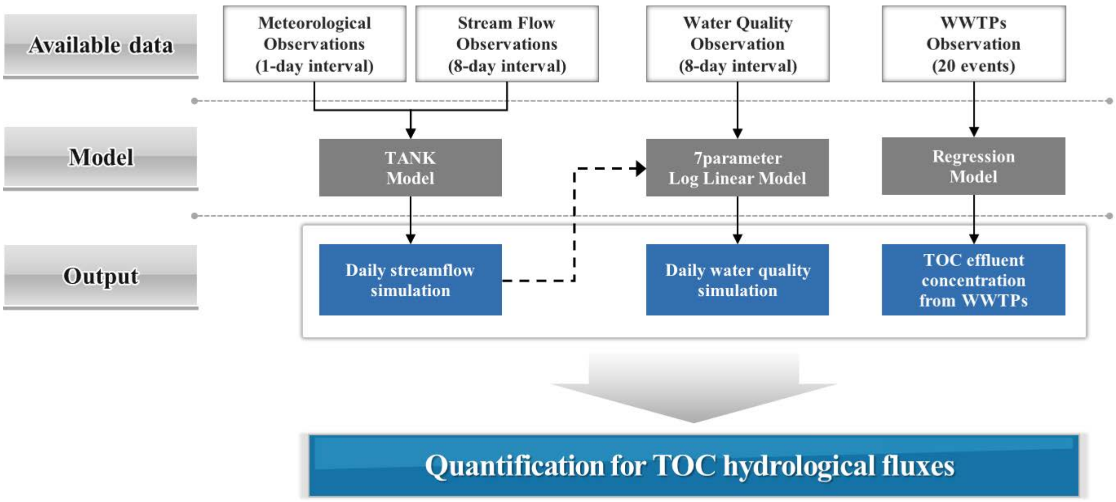


Fig. 3. Schematic diagram for study.

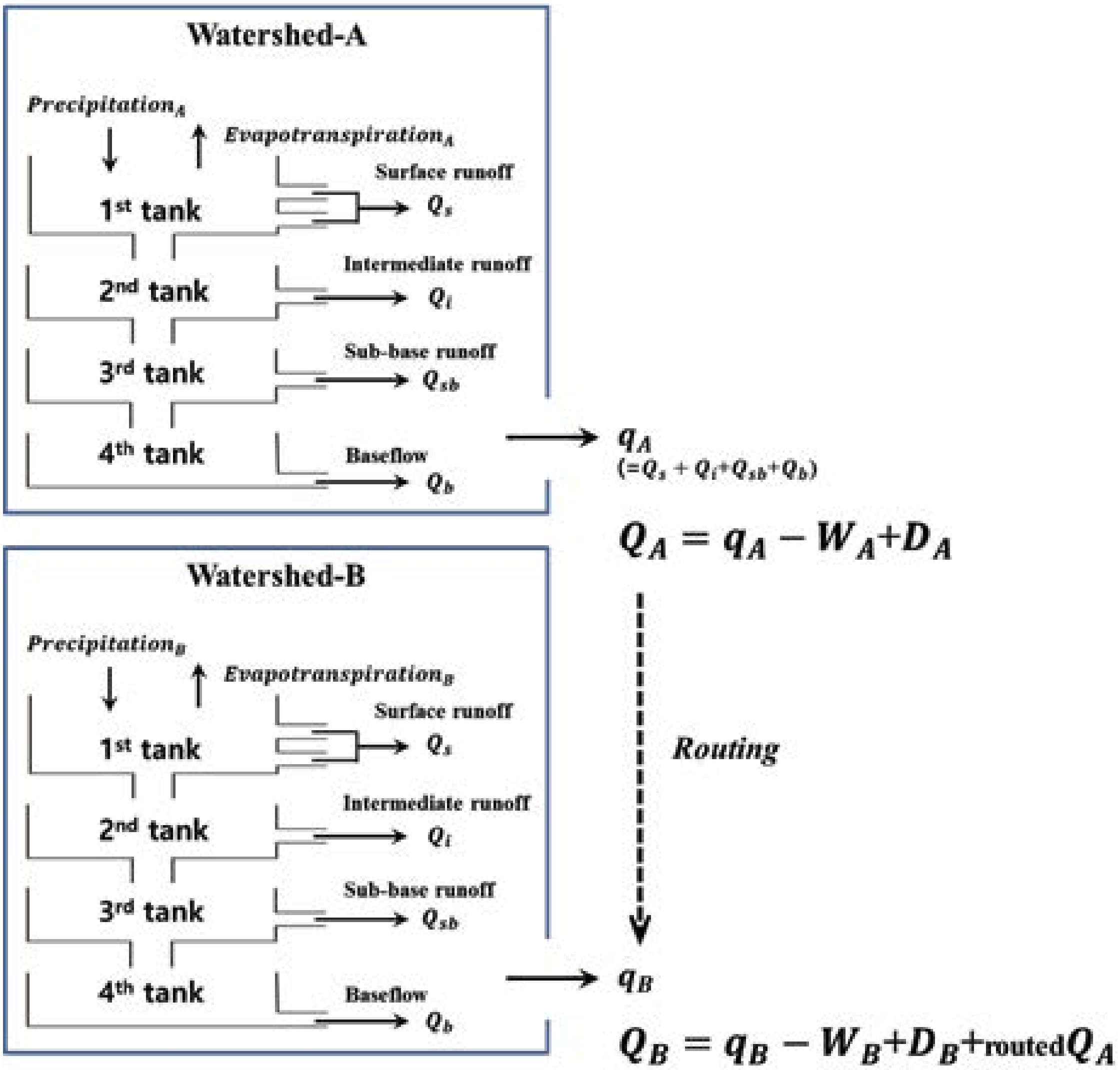


Fig. 4. Conceptual diagram of the revised TANK model.

- The outflow of the 1st stage tank becomes the surface runoff (Q_s)
- From the 2nd tanks, the inflow is equal to the infiltration of the upper tank
- The outflow of the 2nd tank becomes the intermediate outflow (Q_i)
- The outflow of the 3rd tank becomes the unconfined aquifer groundwater discharge (Q_{sb})
- The outflow of 4th tank becomes the confined aquifer groundwater discharge (Q_b)
- The sum of all tank outflow (right direction) is the stream flow

In each sub-basin, the total storage in a channel section, S, is given by Eq. (1) as follows:

$$S = K\left[XI + (1 - X)O\right] \tag{1}$$

where K is the storage constant, O is the outflow, and X is a weighting factor for inflow and outflow ranging from 0.2 to 0.4 in most natural channels. The parameter X is applied to 0.2 and K is calibrated using observed hydrographs and the storage relationship [17].

In Fig. 4, W and D means intaking water volume and discharge from major WWTPs, respectively, which gained by water resource Databases in corresponding watershed.

The actual evapotranspiration (ET) is calculated depending on storage volume (S_t) in the first tank as follows:

$$\text{ET} = \left(1 - e^{-\alpha \times S_t}\right) \times \text{PET} \tag{2}$$

where α is the evapotranspiration coefficient, and the potential evapotranspiration (PET) as input data is calculated by Penman method.

As the TANK model includes many conceptual parameters, proper calibration is essential to simulate the accurate runoff dynamics of a watershed under various climate conditions. The revised TANK model adopted in this study has 18 parameters (5 runoff related coefficients, 3 infiltration related coefficients, the initial and maximum storage of each tank, and the evapotranspiration coefficient and travel time). Since the TANK model has many parameters to be estimated, it cannot accurately estimate the parameters of each tank by a simple mathematical method. Therefore, it is common to estimate those parameters by a trial and error method. Recently, however, the optimization of parameters (e.g., Powell method, Standardized Powell method, Simplex method, Sequential Quadratic Programing (SQP) method, etc.) has been developed in accordance with the development of computer calculation ability [8].

To estimate parameters of the revised TANK model, we used one of the nonlinear optimization method, SQP method [19] under constrained conditions. A SQP algorithm obtains search directions from a sequence of quadratic programming subproblems. Each QP subproblem minimizes a quadratic model of certain Lagrangian function subject to a linearization of the constraints. An augmented Lagrangian merit function is reduced along each search direction to ensure convergence from any starting point [19].

2.5. Daily water quality simulation

Various approaches have been studied to estimate contaminant loads that are transported from non-point sources through stream and river networks. Most approaches are based on the historical relationships between observed stream flow (Q) and contaminant concentration (C) or contaminant loads (L) [10,20–23]. This study adopted the seven-parameter log-linear model developed by USGS to estimate daily loads of TOC [24]. This method has been applied to many watersheds around the world successfully [25–29]. The seven-parameter log-linear model is given by Eq. (3).

$$\ln C = \beta_0 + \beta_1 \ln\left(\frac{Q}{\tilde{Q}}\right) + \beta_2\left[\ln\left(\frac{Q}{\tilde{Q}}\right)\right]^2 + \beta_3\left(T - \tilde{T}\right) + \beta_4\left(T - \tilde{T}\right)^2 + \beta_5 \sin\left(2\pi T\right) + \beta_6 \cos\left(2\pi T\right) + \varepsilon \tag{3}$$

where Q is streamflow, β_0 through β_6 are the parameters of the seven-parameter log-linear model, T is a daily fraction to a year (e.g., T for Jan. 1 = 1/365, T for Jan. 2 = 2/365, etc.), ε is a model's tolerance, and $\tilde{T}$ is expressed by Eq. (4).

$$\tilde{T} = \bar{T} + \frac{\sum_{i=1}^{n}\left(T_i - \bar{T}\right)^3}{2\sum_{i=1}^{n}\left(T_i - \bar{T}\right)^2} \tag{4}$$

where $\bar{T}$ is the mean of T.

When estimating the parameters of Eq. (3) by simple regression analysis, the estimated load tends to show bias. The bias in the regression-estimated load can result when the value is retransformed from log space to linear space [30]. Previous study compared the traditional simple linear regression estimator, the quasi maximum likelihood estimator, and the Minimum Variance Unbiased Estimator (MVUE) and introduced MVUE as a more accurate estimator [10]. Therefore, the MVUE is adapted to estimate parameters β_i of the seven-parameter log-linear model for correcting the bias induced by log transformation. The MVUE procedure is discussed in the studies of Han et al. [10] and Bradu and Mundlak [31]. Once parameters are estimated, the daily water quality (TOC) loads can be simulated at each sub-basin by combining the seven-parameter log-linear model and stream flow data simulated by the revised TANK model (Section 2.2).

2.6. TOC effluent concentration from WWTPs

To quantify the contribution of TOC point sources at a watershed scale, the load of the TOC point sources within the watershed must be estimated. However, most WWTPs in South Korea typically only hold the effluent BOD and COD data. Since the daily discharge flow and water quality of WWTPs are almost constant, TOC was estimated through multiple regression analysis with BOD and COD as independent variables. Even though it is more reasonable that the concentration of TOC is estimated by multiple regression including particulate organic matter such as SS, given the availability of data provided, it is judged to be valid that the concentration of TOC is estimated by multiple regression using the concentration of BOD and COD. In this study, the effluent BOD, COD and TOC concentrations discharged from the selected WWTPs (Gumi, Sincheon, Dalseo Seobu and Seongseo) have been monitored, since these WWTPs were thought to represent point sources of the Nakdong River basin. Using monitored BOD, COD and TOC concentration data (Table 1), the multiple regression formula to estimate the concentration of TOC emission from the concentration of BOD and COD emission can be determined. Using the regression formula to be constructed, it is possible to estimate the daily TOC point sources loads for each sub-basin. The hydrologic flux of TOC and the load of the TOC point sources for each sub-basin can be used to examine the contribution of point sources by sub-basin.

3. Results and discussion

3.1. Daily stream flow simulation results

Fig. 5, as an example of simulation results, shows observed stream flow and simulated stream flow at NB-D and NB-I in the Nakdong River mainstream. In the top column, *P* means daily precipitation (mm/d), and the dotted line means potential evapotranspiration (mm/d), the line means actual evapotranspiration (mm/d) in the middle column. In the bottom column, *Q* indicates daily stream flow and the line is simulated stream flow and the points mean observed stream flow. The figure shows that the TANK model effectively simulates the actual evapotranspiration and river flow.

Fig. 6 shows the calibrated storage constant *K* for the Muskingum river routing process. It ranges from 0.3 to 0.5 d^{-1} depending on sub-basins.

For more quantitative assessment of model accuracy, the determinant coefficient and the model efficiency coefficient (NSC) suggested by Nash and Sutcliffe [32] were applied between observations and simulations. Fig. 7 shows the R^2 and NSC results of the TANK model applied to the Nakdong River basin. As a result, the determinant coefficient was 0.82 on average, and the model efficiency coefficient was 0.77 on average. Therefore, observed stream flows were thought to have been excellently reproduced.

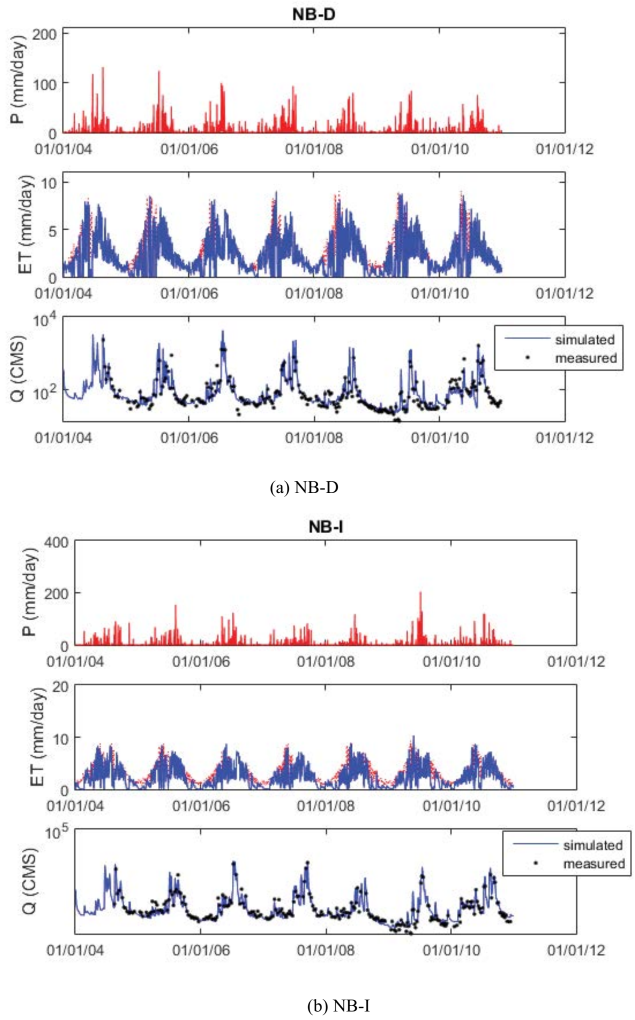


Fig. 5. Calibration and verification of the revised TANK model: (a) NB-D and (b) NB-I.

Table 1
Monitored data of wastewater treatment plants

Site	Monitoring period	Number of sampling events	Range of values (mg/L)		
			BOD	COD	TOC
GM (Gumi)	01/04/2011–05/25/2011	3	2.15–4.16	8.88–10.08	3.54–6.81
SC (Sincheon)		3	3.56–5.58	6.63–8.99	4.20–5.11
DS domes. (Dalseo)		3	0.90–1.53	14.13–18.57	11.96–13.08
DS Indus. (Dalseo)		3	1.04–1.86	17.03–22.40	14.22–17.01
DS Total (Dalseo)		3	2.42–5.16	11.02–12.96	12.51–13.06
SB (Seobu)		3	2.52–3.91	7.88–9.45	4.71–7.28
SS (Seongseo)	03/28/2011–05/25/2011	2	3.43–6.51	11.12–11.74	8.14–9.33

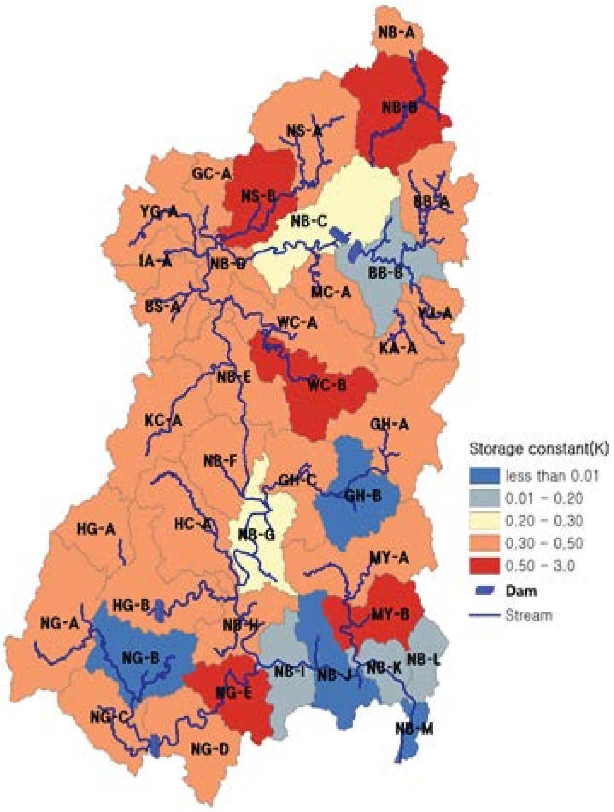


Fig. 6. Calibrated storage constant (*K*) for sub-basins.

3.2. Daily water quality simulation results

Based on simulated daily stream flow data, daily TOC loads were simulated through linkage between the seven-parameter log-linear model. Fig. 8, as an example of simulation results, shows observed TOC loads and simulated TOC loads at NB-D and NB-I in the Nakdong River mainstream. In figure, the horizontal axis shows observed TOC load (kg/day) and the vertical axis means calculated TOC load (kg/d). As a result of TOC load estimation, the determinant coefficient was 0.96 on average. Therefore, it can be seen that observed TOC loads can be successfully simulated.

3.3. TOC effluent concentration from WWTPs

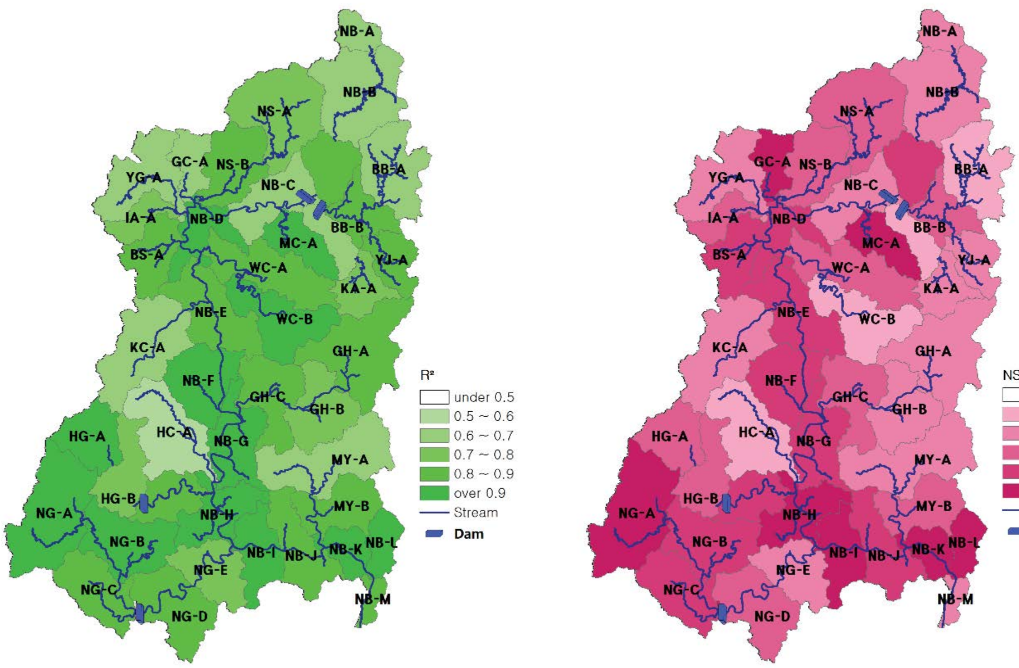
The regression analysis between BOD, COD and TOC effluent concentration (mg/L) data monitored from major WWTPs (GM, SC, SB, SS and DS) was performed and the regression equation yielded as follows:

$$\text{TOC} = -3.9078 + 0.5375\ \text{BOD} + 0.9394\ \text{COD} \quad (5)$$

The coefficient of determination between the simulated TOC by Eq. (5) and the observed TOC was 0.79 (see Fig. 9). Due to its statistical significance in correlation, it can be assumed that the TOC effluent concentration of WWTPs is acceptable for consequent analysis.

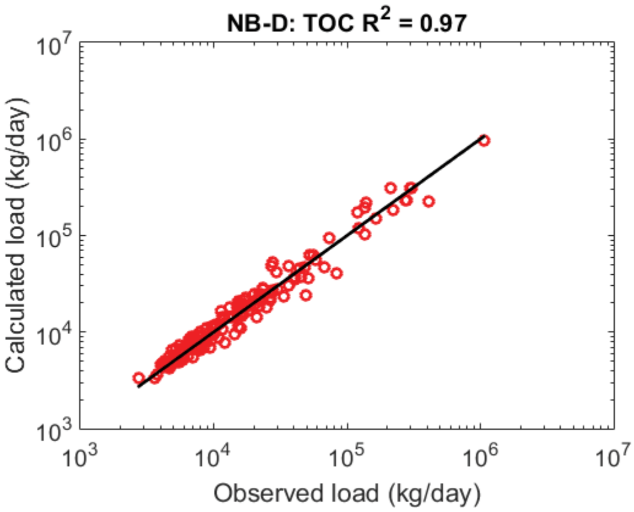
3.4. Spatio-temporal analysis of TOC hydrologic fluxes

Figs. 10 and 11 show seasonal daily TOC loads and concentrations at outlet of each TMDL sub-basin. The load

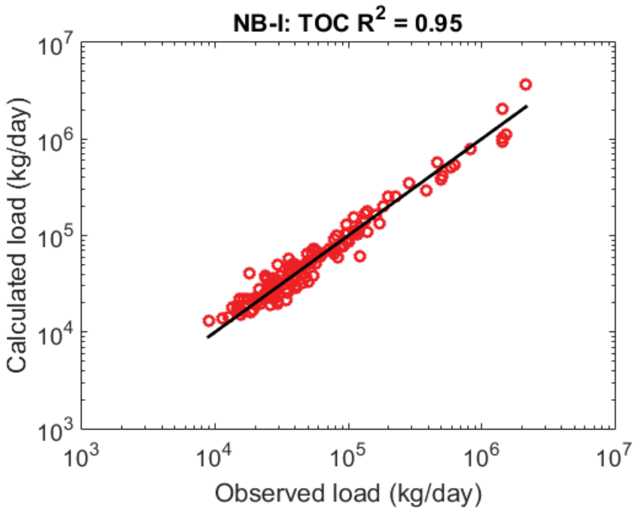


(a) NB-D (b) NB-I

Fig. 7. Results for R^2 and NSC: (a) NB-D and (b) NB-I..



(a) NB-D



(b) NB-I

Fig. 8. Results for TOC load simulation: (a) NB-D and (b) NB-I.

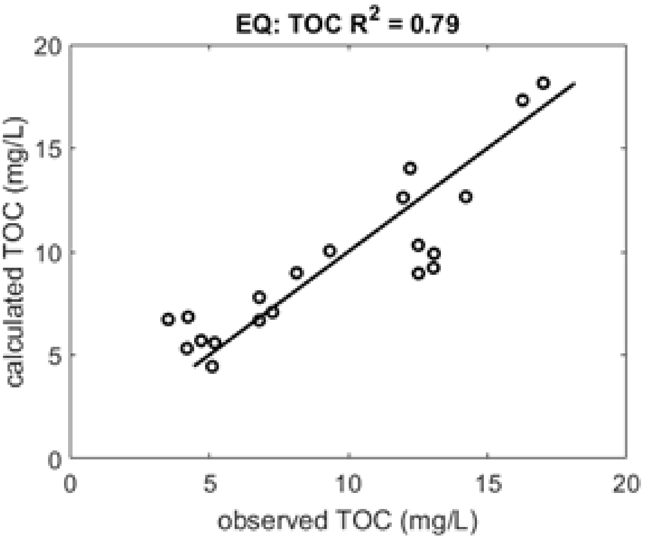


Fig. 9. Result of TOC regression model compared with the observed.

of TOC point sources within each sub-basin is shown in Fig. 12.

As a result of analyzing the spatial pattern of TOC load (Fig. 10), it can be seen that the TOC loads are increasing in the downstream direction. In the case of the temporal pattern, TOC loads in summer are the largest when compared with other seasons, and TOC loads in winter are relatively small. This means that the TOC load is proportional to the precipitation in the Nakdong River basin, and a significant amount of the TOC hydrologic flux is emitted in the form of non-point pollutants.

The spatial pattern of the TOC concentration (Fig. 11) is similar to the spatial pattern of the loading, and the concentration increases in the downstream direction. Regardless of the season, WC-A, WC-B, GH-C, MY-A, MY-B and NB-M sub-basins show high TOC concentration. Of these, the high concentrations of WC-A and WC-B are considered to be influenced by the large industrial complex, and the high concentration of GH-C is considered to be influenced by industrial wastewater and domestic sewage from Daegu Metropolitan. The high concentrations of TOC in the upper sub-basins of the Nakdong River basin in summer are analyzed as the effect of non-point pollution sources.

The analysis of TOC point sources shows that the largest amount of point pollutants is emitted from GH-C (Fig. 12). This is because many pollutant loads are discharged from various industrial complexes and sewage treatment plants existing in GH-C.

The contribution of point sources load was investigated by using the hydrologic flux and the point sources load of TOC for each sub-basin (Fig. 13). The contribution of point sources is calculated as the ratio of TOC load of environmental facilities and TOC hydrological flux to the cumulative sum from upstream to downstream for each sub-basin.

It was found that the contribution of TOC point sources on the hydrologic flux throughout the Nakdong River basin was highest in the winter season, and decreased in the order of autumn, spring and summer. This implies that precipitation greatly affects the hydrologic flux of TOC emitted from the watershed. In terms of sub-basin, GH-B and GH-C show very high contribution of point sources except for the summer season, which is considered to be the influence of point sources emitted from Daegu Metropolitan. In the case of the mainstream of Nakdong River, it can be seen that the contributions of point source are greatly changed before and after Geumho River (GH-A, GH-B and GH-C) joins. This means that the mainstream of the Nakdong River should be managed differently before and after the confluence of Geumho River. Also, since high contribution of point sources in NS-A and BS-A, which are upper sub-bains in the Nakdong River basin, was found in all seasons

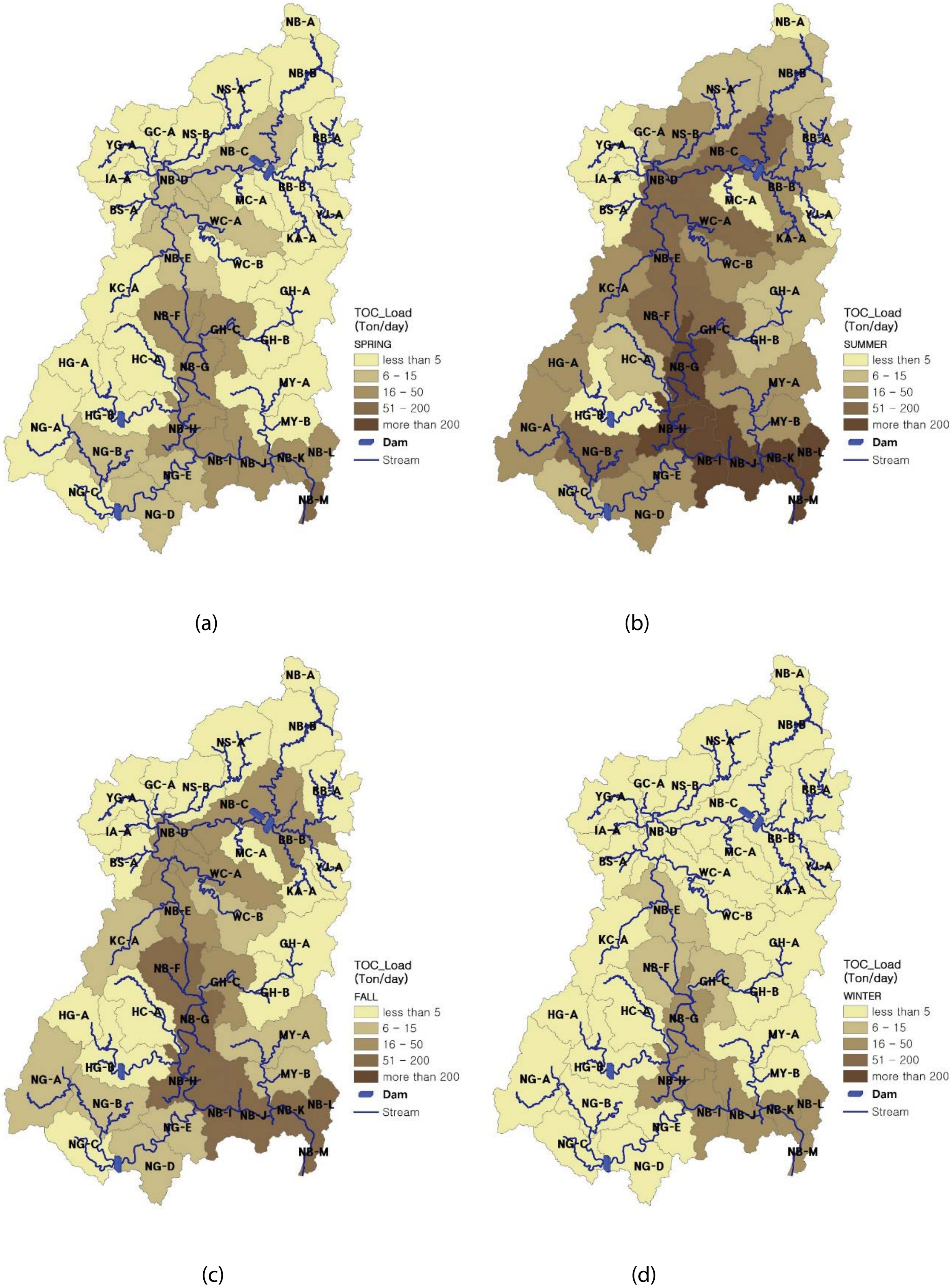


Fig. 10. TOC load: (a) spring, (b) summer, (c) fall and (d) winter.

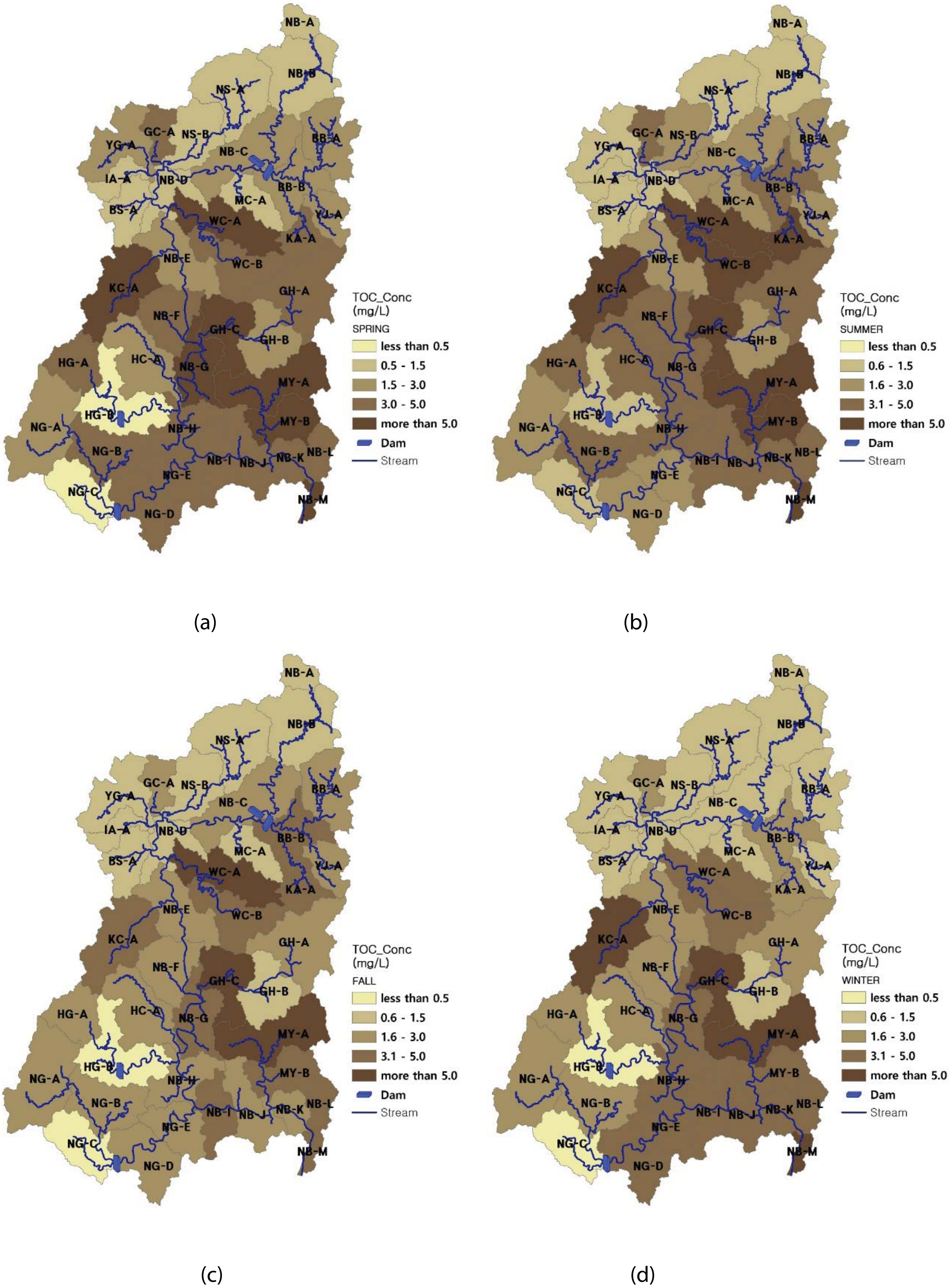


Fig. 11. TOC concentration: (a) spring, (b) summer, (c) fall and (d) winter.

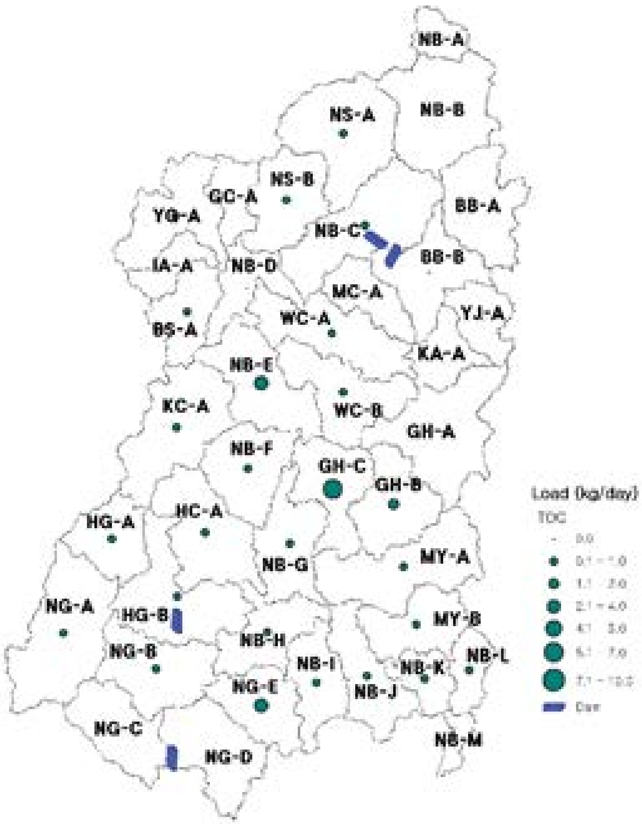
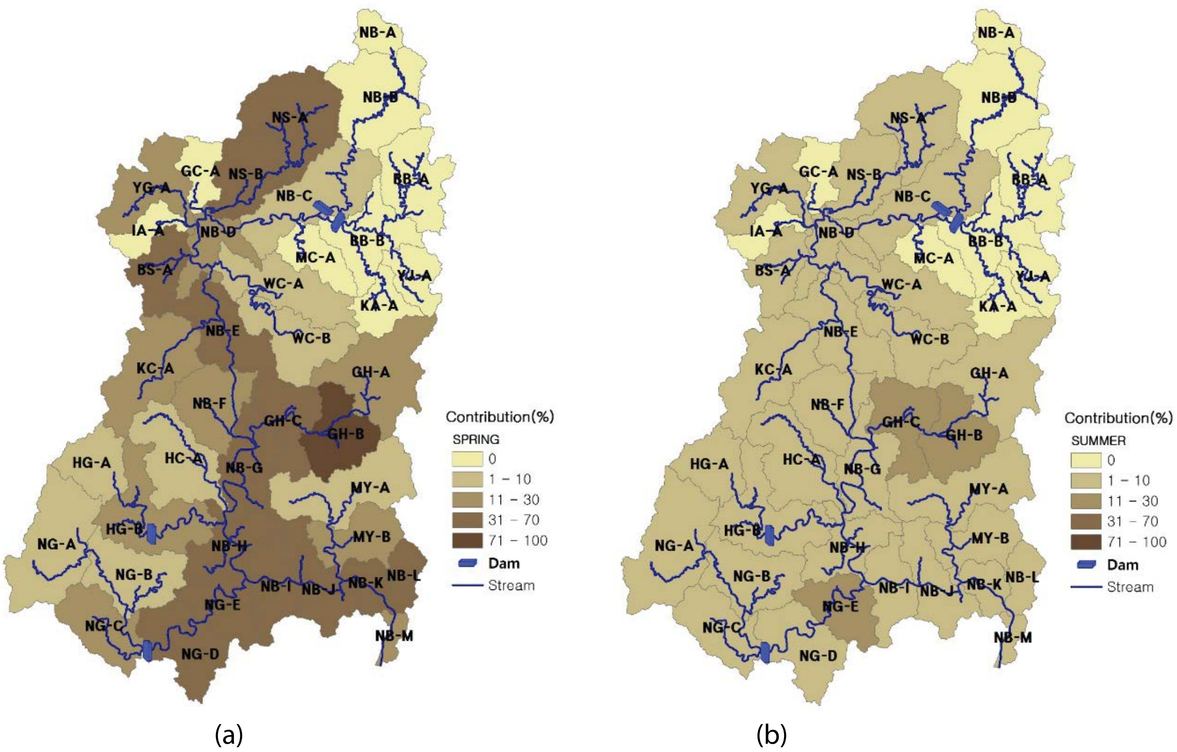


Fig. 12. TOC point source load.



(Fig. 13 continued)

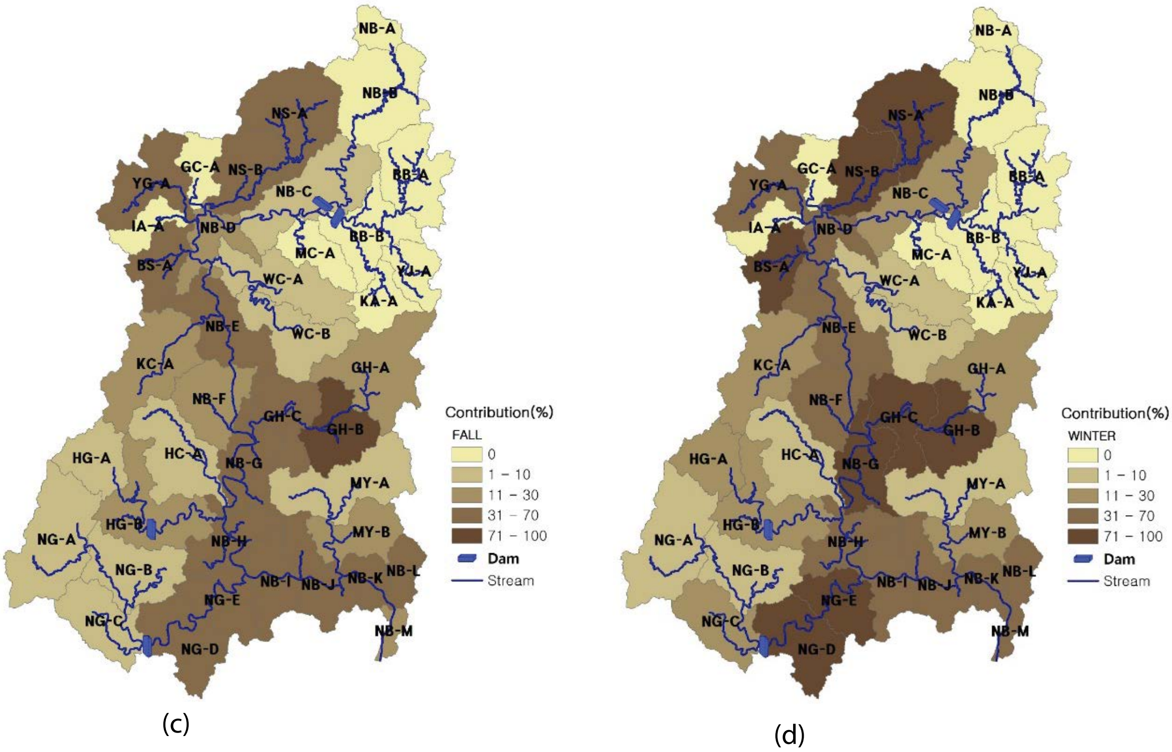


Fig. 13. Contribution of TOC point sources: (a) spring, (b) summer, (c) fall and (d) winter.

except the wet season, it is urgent to manage point sources in these sub-basins. In addition, the contributions of point sources in NG-C, NG-D, NG-E and NG-F sub-basin are relatively high compared with other sub-basins.

4. Conclusion

This study aims to propose a simple but reliable methodology to investigate the hydrological flux of TOC in the watershed scale by linking a series of modelling techniques that simulate daily streamflow and water quality. The revised TANK model and the seven-parameter log-linear model were applied to extend the 8-d interval observations to daily data. Regression analysis using BOD, COD and TOC data was also performed to obtain TOC information from the effluent of major WWTPs, which only provided the information on BOD and COD. Based on the calculated daily flow and water quality and TOC point source load, the temporal and spatial variations of TOC hydrologic fluxes in the watershed scale were examined.

The hydrologic fluxes of TOC in the Nakdong River basin tended to increase the downstream direction, so the hydrologic flux of TOC thought to be significantly affected by rainfall. In addition, it was confirmed that the water quality management strategy of the mainstream of the Nakdong River should be approached differently before and after Geumho River, where point sources pollutant emissions are very high, joins.

This methodology is expected to provide reasonable results even in watersheds with insufficient observation data, since the spatial and temporal variation of TOC hydrologic fluxes can be examined by conceptualizing the watershed using discontinuous observation data. It is important to note that the 8-d interval observations used in this study may not adequately reflect the behaviour of the organic matter during the rainfall event, and there is a limitation that the uncertainty of the data can be increased in the process of reproducing the daily data. This means that the organic matter load introduced by the nonpoint source is likely to be underestimated relatively. Therefore, it is reasonable to conclude that the contribution of the point sources in summer is the maximum contribution of the point sources. However, when the related research results [10,11,28] are examined, the results of this study are thought to be have sufficient reliability.

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Symbols

$\bar{T}$ — Mean of T in the seven-parameter log-linear model
BOD — Biological oxygen demand
C — Concentration
COD — Chemical oxygen demand
ET — Actual evapotranspiration
K — Storage constant in the Muskingum routing method

O	—	Outflow in the Muskingum routing method
PET	—	Potential evapotranspiration
Q	—	Streamflow
S	—	Total storage in the Muskingum routing method
S_t	—	Storage volume in the tank
T	—	Daily fraction to a year in the seven-parameter log-linear model
TOC	—	Total organic carbon
X	—	Weighting factor for inflow and outflow in the Muskingum routing method
α	—	Evapotranspiration coefficient
β_0–β_6	—	Parameters of the seven-parameter log-linear model
ε	—	Model's tolerance in the seven-parameter log-linear model

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