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Trend Analysis Using Long-Term Monitoring Data of Water Quality at Churyeongcheon and Yocheon Basins

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Abstract: In this study, we investigated the interrelationships between organic matter and water quality indices in the total maximum daily load basins, namely, Churyeongcheon and Yocheon of the Seomjin River system, and identified trends. Churyeong A and Yocheon B, the basins being analyzed, have high proportions of nonpoint pollution sources and pollutant loads from terrestrial sources. During the study period, biochemical oxygen demand (BOD) decreased in both basins, whereas chemical oxygen demand (COD) and total organic carbon (TOC) increased in Churyeong A and decreased in Yocheon B. The increase in organic matter in Churyeong A correlated with the flow rate, whereas organic matter in Yocheon B showed little correlation with flow rate. Variations in organic matter (BOD, COD, and TOC) in Churyeong A exhibited seasonality under the influence of increased flow rate. Organic matter in Yocheon B was affected by increased flow rate, wherein with time, BOD decreased and COD and TOC increased. This study provides basic data that can be used as a reference to facilitate continuous water management and appropriate strategy implementation by analyzing the influencing factors and trends of organic matter using long-term measurement data.

Keywords: total maximum daily load; tributary monitoring; pollutant loads; regression model; LOAD ESTimator model; water quality; climate change

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1. Introduction

River networks are influenced by external factors such as climate and tectonic activity and serve as primary pathways for the movement of sediment, water, and other environmental fluxes. These fluxes become a part of various ecosystems in a river basin thereby supporting ecological activities. Significant threats are posed by climate and anthropogenic activities to river networks. Understanding the topologic structure and dynamics of river networks is essential to monitoring the dynamics of changes in the fluxes and their influencing factors, and for better environmental management [1].

Biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) are indicators of organic matter in water systems. They react with chlorine in water sources, generally in the upstream river system, and produce carcinogenic disinfection byproducts. Organic matter is managed through several systems. Currently, water quality management in South Korea is progressing. Previous research has shown that after the setting up of sewage treatment and water purification plants, BOD and oxygen depletion reduced in a river, whereas COD and TOC increased [2].

Typically, a large proportion of organic matter in rivers originates from land. Sun-Hye (2015) found that in river systems, the proportion of organic matter of natural origin (derived from plants) reached 81% in river sections surrounded by forest soil with upstream measurement points [3]. In addition, the proportions of various anthropogenic organic matter originating from humans and livestock gradually increased further downstream [3].

As most of South Korea is forest land with steep mountainous terrain, the rate of soil and sediment runoff, mainly due to localized heavy rain during the rainy season, is high. Particularly, as rainfall intensity gradually increases due to climate change, the amount of soil and sediment runoff into basins gradually increases [3,4]. Organic matter in river systems increases with the inflow of runoff soil and sediment containing organic matter (degradable and persistent) that has undergone decomposition by microorganisms [3,4].

According to Shang et al. [5], dissolved organic carbon and dissolved organic matter in aqueous ecosystems are associated with organic matter. Recently, studies by Sarker [6] and others have stated that it is difficult to manage organic pollution because of the diversity of their origin and characteristics of decomposition rate. TOC is an indicator of organic pollution levels; however, it is difficult to manage due to the variety of organic matter sources and the characteristics of corresponding decomposition rates.

The total maximum daily load (TMDL) is the estimation of the maximum amount of a pollutant that can be allowed to enter a waterbody, such that quality standards for that particular pollutant can be maintained in the waterbody. This estimate sets the target for the reduction of a particular pollutant such that their sources can be controlled. In this study, long-term observation data of the total maximum daily load (TMDL) were used to assess organic contamination to reflect the achievement of the target by allocating pollutants with respect to watersheds. The aim of this study was to examine the interrelationships between organic matter (BOD, COD, and TOC) and water quality indices, and identify trends that could provide baseline data, which could facilitate continuous water management and implementation of a suitable strategy.

2. Materials and Methods

2.1. Study Area

The study areas selected were Churyeongcheon and Yocheon, which are representative tributaries located upstream in the Seomjin River and Jeollabuk-do. The basin area of Churyeongcheon is 152.3 km^2 and consists of 72.9% forest land, 18.1% agricultural land, and 1.2% sites. The basin area of Yocheon is 487.3 km^2 and consists of 67.7% forest land, 16.6% agricultural land, and 2.1% sites. The Namwon Sewage Treatment Plant, which has a treatment capacity of 50,000 m^3/day, is in the downstream basin of Yocheon.

Churyeongcheon and Yocheon have 1 and 2 TMDL unit basins, respectively. A monitoring network operates at the end of both basins, where the flow rate and water quality are measured at intervals of approximately 8 days. Figures 1 and 2 show monitoring network unit basins and land cover map, respectively. Table 1 shows the classification of soil phase shown in Figure 2, and Table 2 shows the status and target water quality of the unit basins.

Table 1. Land use category codes.

Name	Major Classification	Middle Classification	Name	Major Classification	Middle Classification
AGRL	Agriculture land	Agriculture	UCOM	Used area	Urbanization Commercial area
ORCD		Orchard	UIDU		Urbanization Industrial area
RICE		Rice fields	UINS		Urbanization Institutional area
FRSD	Forest	Forest deciduous	URML		Urbanization Residential area
FRSE		Forest evergreen	UTRN		Urbanization Transportation area
FRST		Forest intermixture	WATR	Water	Water
RNGE	Grass	Grassland	WETL	WETL	Wetland
SWRN	Barren	Barren			

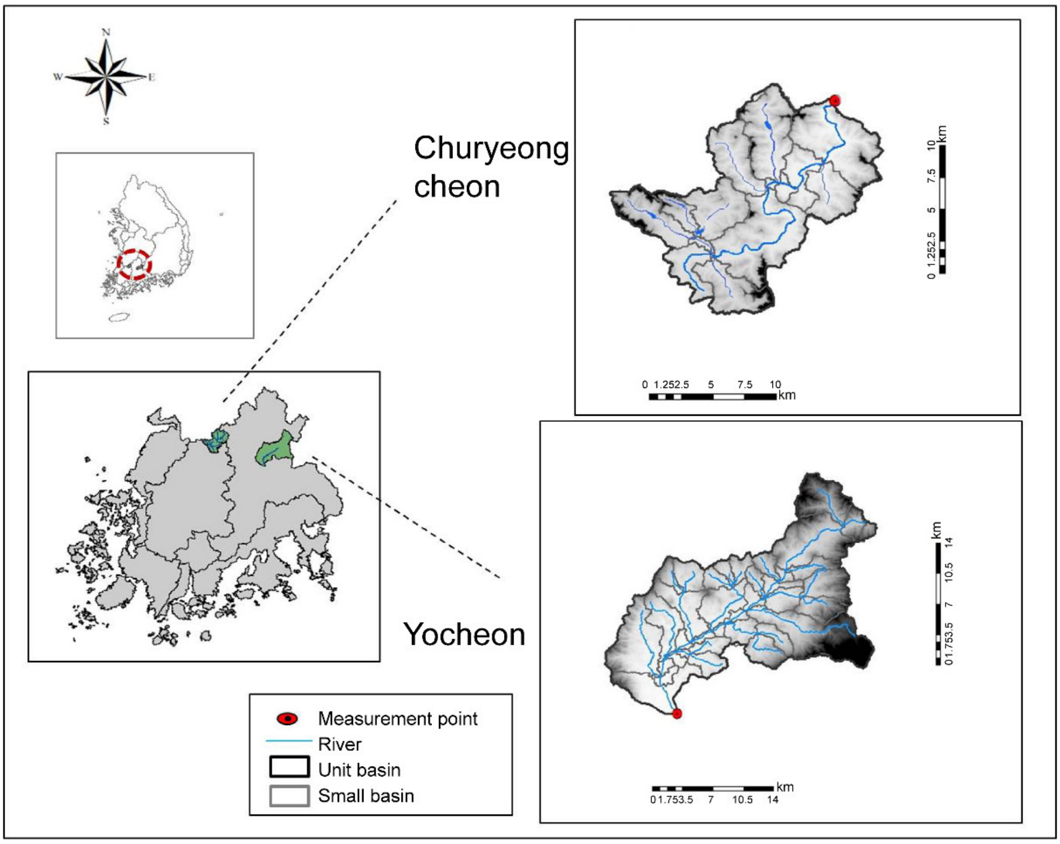

Figure 1. Locations of the measurement points in Churyeongcheon (**top**) and Yocheon (**bottom**).

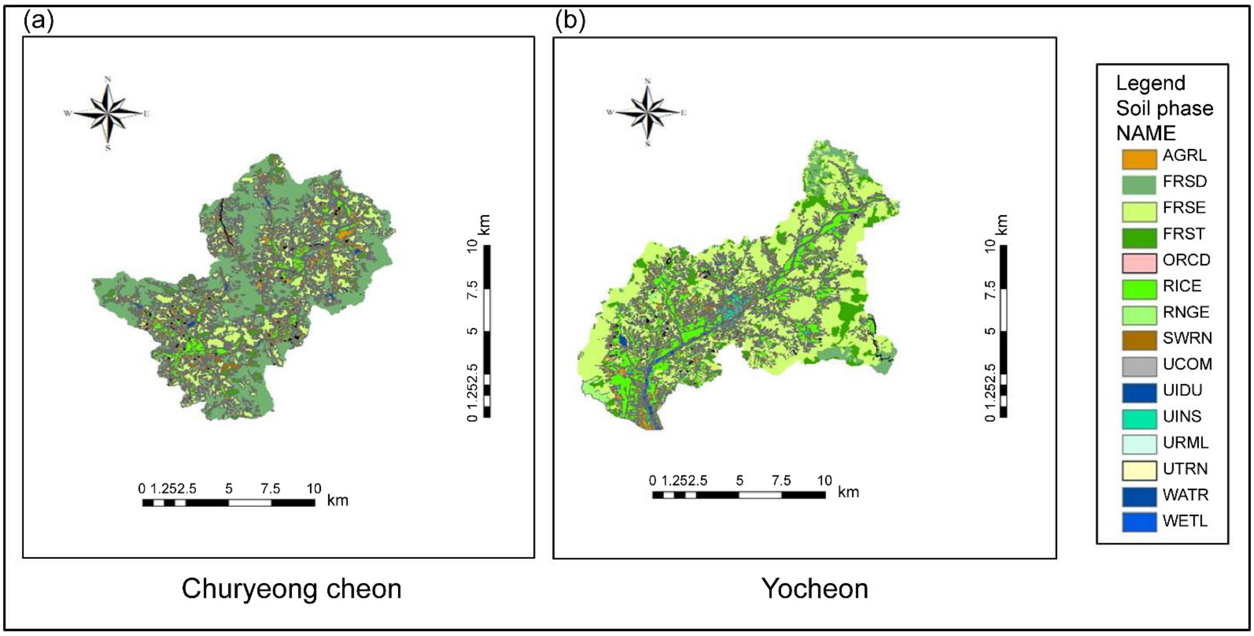

Figure 2. Soil phases of the measurement points in (**a**) Churyeongcheon and (**b**) Yocheon.

Table 2. Characteristics of the study areas. Data sourced from: 3rd Master Plan for Quantity Regulation of Water Pollution in Jeollabuk-do Seomjin River, Jeollabuk-do ('16).

Tributary	Administrative District	Area (km^2)	Total Channel Length (km)	No. of TMDL Basins	No. of Sub-Basins	Total Number of Nodes	3rd Phase ('16–'20) Target Water Quality (mg/L)	
							BOD5	TP
Churyeongcheon	Sunchang County in Jeollabuk-do	152.3	37.0	1	3	8	1.1	0.018
Yocheon	Namwon city and Jangsu County in Jeollabuk-do	487.3	60.030	2	13	23	1.5	0.063

2.2. Water Quality and Flow Rate Conditions

Water quality and flow rate conditions were analyzed based on data from 2011 to 2020 for the Churyeong A and Yocheon B monitoring network points at the end of Churyeongcheon and Yocheon. In the present study, pollutant loads of the unit basins were divided into 3-year intervals and their increase or decrease was determined to analyze the characteristics of water quality changes.

2.3. Water Quality Correlation Analysis

Using the observed flow rate and water quality data, a correlation analysis was performed to determine the relationships among water quality factors and to identify the water quality characteristics of the target basins. Data were not normally distributed (Kolmogorov–Smirnov significance probability, $p > 0.05$). However, the absolute values for skewness and kurtosis of the descriptive statistics did not exceed two, except for SS, EC, and flow rate, indicating significance. A correlation analysis was carried out using the Pearson correlation analysis [7].

2.4. Seasonal Kendall Tests

A nonparametric statistical method that analyzes trends through correlation measures between observations was used to independently perform a Kendal test for each season and then derive a Kendall statistical estimate through the weighted sum of each result [8–10].

Equation (1) is the Mann–Kendall equation for each season. Here, Sgn (season) = 1, 2 . . . , p [9].

$$S_g = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} Sgn(X_{jg} - X_{ig}) \quad (1)$$

Equation (2) calculates the sum of Kendall's S statistics by dividing data by month and season in the seasonal Kendall test, which is an extension of the Mann-Kendall test.

The seasonal Kendall statistic is:

$$\dot{S} = \sum_{g=1}^{p} S_g. \quad (2)$$

Equation (3) applies when the sample is large (n > 10) [11], where μ_{SK} (average) and $V_{ar}(S^*)$ (variance) are approximated to normal distribution.

$$\mu_{SK} = 0$$

$$V_{ar}(S^*) = \sum_i V_{ar}(S^*) = \frac{\sum_i [n_i(n_i - 1)(2n_i + 5)]}{18} \quad (3)$$

Equation (4) is applied when there are several data representing the same value, categorized into groups and substituted below, and applied when the average is 0 and n > 10.

$$V_{ar}(S^*) = \sum_i V_{ar}(S^*) = \sum_i [n_i(n_i - 1)(2n_i + 5)] - \sum_{t_i} t_i(t_i - 1)(2t_i + 5)]/18$$

$$Z_{SK} = \left\{ \begin{array}{cc} \frac{S^{*}-1}{\sqrt{Var(S^{*})_{SK}}} & S_K > 0 \\ 0 & S_K = 0 \\ \frac{S^{*}+1}{\sqrt{Var(S^{*})_{SK}}} & S_K < 0 \end{array} \right\} \tag{4}$$

Standardized Z statistics using $Var(S^{*})$ were applied. Here, n_i is the number of data in the season, t_i is the number of tied group ($|Zsk| > Z\alpha/2$ rejects the null hypothesis), where the null hypothesis H0: slope $\widetilde{b}_i = 0$ (not trend), is obtained and the Z statistic and *p* value were determined to obtain water quality trends.

2.5. LOADEST Model

A regression-based LOAD ESTimator (LOADEST) model, developed by the United States Geological Survey (USGS), was used to evaluate the characteristics of long-term load changes in Churyeongcheon and Yocheon [12]. The LOADEST model provides 11 regression models for evaluating pollutant loads; in the present study, we applied the multivariate log-linear model [13]. In Equation (5), the regression equation requires seven coefficients. Through the seven predicted coefficients, the flow rate dependence, temporal trends, and seasonality of pollutant loads can be evaluated.

$$\begin{aligned} &\ln y \\ &= a_0 + a_1 \ln Q + a_2 \ln\ Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5 dtime \\ &+ a_6 dtime^2 \end{aligned} \tag{5}$$

where, y is the pollutant load, lnQ is the logarithmic flow rate minus the center of these values, dtime is the value obtained by converting the time of year to a decimal between 0 and 1 minus the center of these values, and a0 to a6 are regression coefficients. Cohn et al. presented a detailed method for calculating the center [13].

Nash–Sutcliffe efficiency (NSE), percent BIAS (PBIAS), and root mean square error-observation standard deviation ratio (RSR) were used to evaluate the load simulated by the regression model, which are presented in Equations (6)–(8). The four performance ratings based on monthly data, proposed by Moriasi et al., were applied to evaluate the fit for each statistical variance (Table 3) [14].

$$NSE = 1 - \frac{\sum (Qobs - Qcal)^2}{\sum (Qobs - \overline{Qobs})^2} \tag{6}$$

$$PBIAS = 1 - \frac{\sum (Qobs - Qcal)^2 \times 100}{\sum Qobs} \tag{7}$$

$$RSR = \frac{RMSE}{STDEV} = 1 - \frac{\sqrt{\sum (Qobs - Qcal)^2}}{\sqrt{\sum (Qobs - \overline{Qobs})^2}} \tag{8}$$

where, Q_{obs} is the observation data, Q_{cal} is the prediction data, and $\overline{Qobs}$ is the mean value of the observation data.

Table 3. General performance ratings for recommended statistics Adapted with permission from Ref. [14]. Copyright year: 2007, copyright owner: Transactions of the ASAE.

Performance Rating	NSE	PBIAS (%)	RSR
Very good	$0.75 < NSE \leq 1.0$	$PBIAS < \pm 10$	$0.00 < RSR \leq 0.5$
Good	$0.65 < NSE \leq 0.75$	$\pm 10 \leq PBIAS < \pm 15$	$0.50 < RSR \leq 0.6$
Satisfactory	$0.50 < NSE \leq 0.65$	$\pm 15 \leq PBIAS < \pm 25$	$0.60 < RSR \leq 0.7$
Unsatisfactory	$NSE \leq 0.50$	$PBIAS > \pm 25$	$RSR > 0.7$

3. Results

3.1. Water Quality, Flow Rate, and Pollutant Load Characteristics

The average flow rate in Churyeong A from 2011 to 2020 was 3.267 m^3/s. The maximum flow rate was 55.528 m^3/s (2012), and the minimum flow rate was 0.183 m^3/s (2011). BOD and TOC ranged from 0.4 to 1.8 mg/L and 0.200 to 4.400 mg/L, respectively (Table 3 and Figure 3).

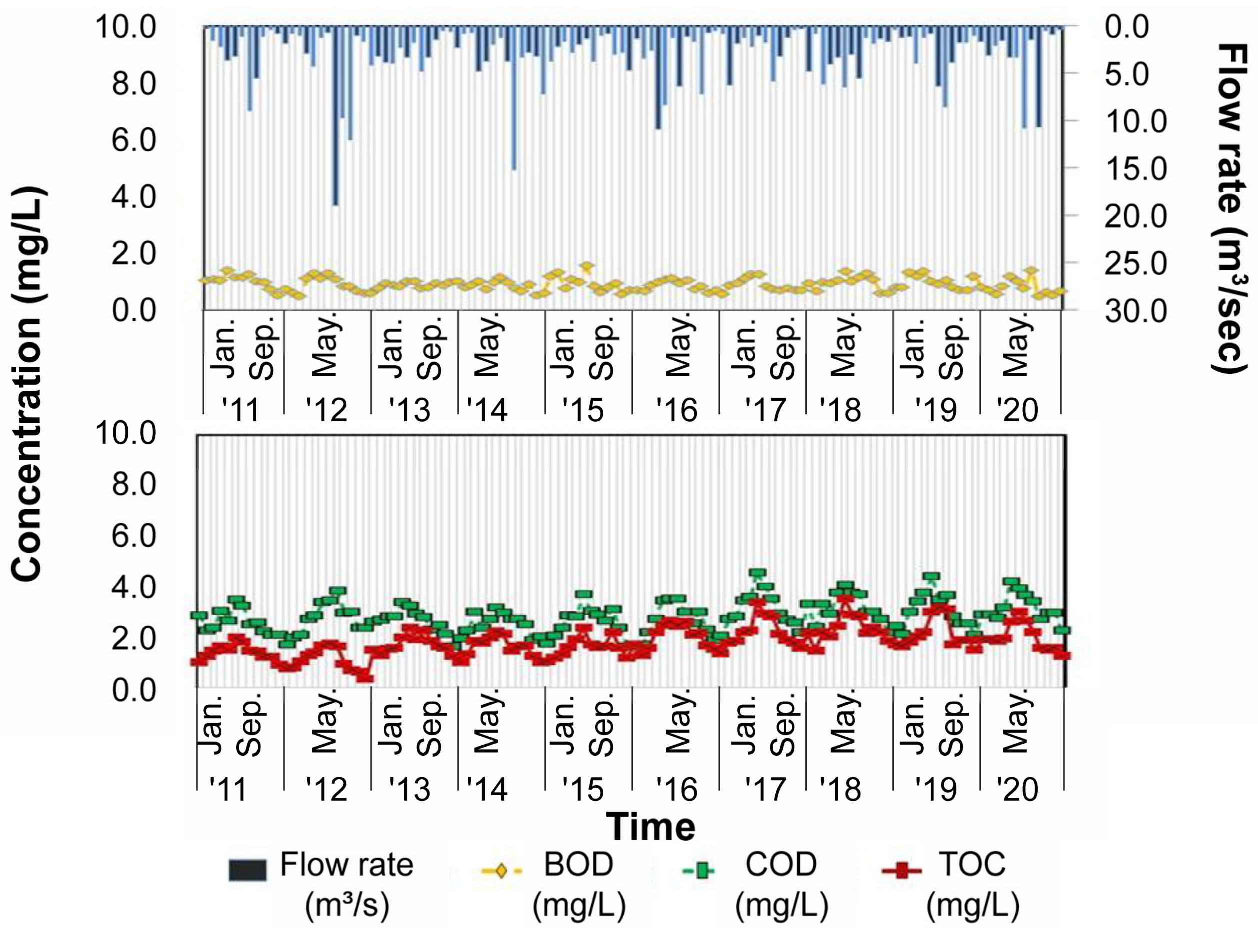

Figure 3. Measurement data of flow rate and water quality (biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) in Churyeong A from 2011 to 2020.

The organic matter items were analyzed using the following methods: diagram electrode method for BOD, $KMnO_4$ method for COD, and a combination method for TOC according to the water quality process test standard. In addition, TN and TP were analyzed using continuous flow analysis, and EC was analyzed using portable field meters.

The average flow rate in Yocheon B was 7.011 m^3/s. The maximum flow rate was 93.660 m^3/s (2012), and the minimum flow rate was 0.327 m^3/s (2017). BOD and TOC were 0.5–4.7 mg/L and 0.900–8.500 mg/L, respectively (Figures 4 and 5).

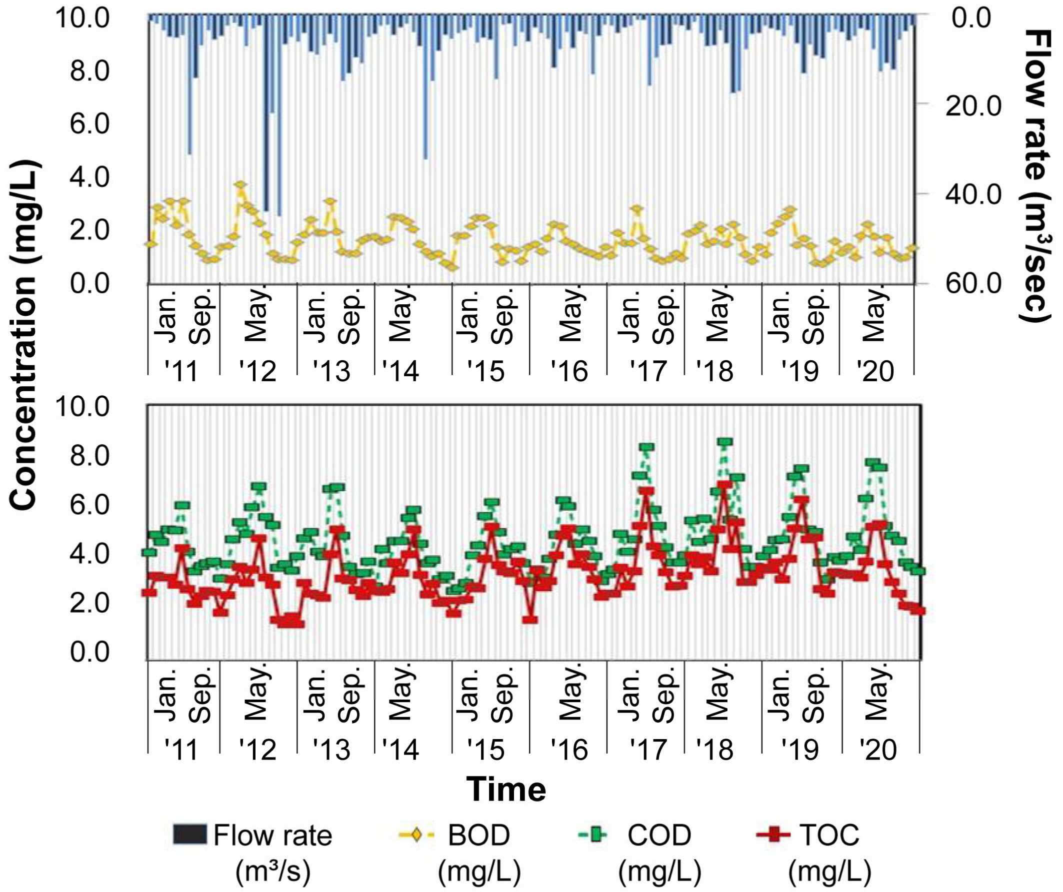

Figure 4. Measurement data of flow rate and water quality (biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) in Yocheon B from 2011 to 2020.

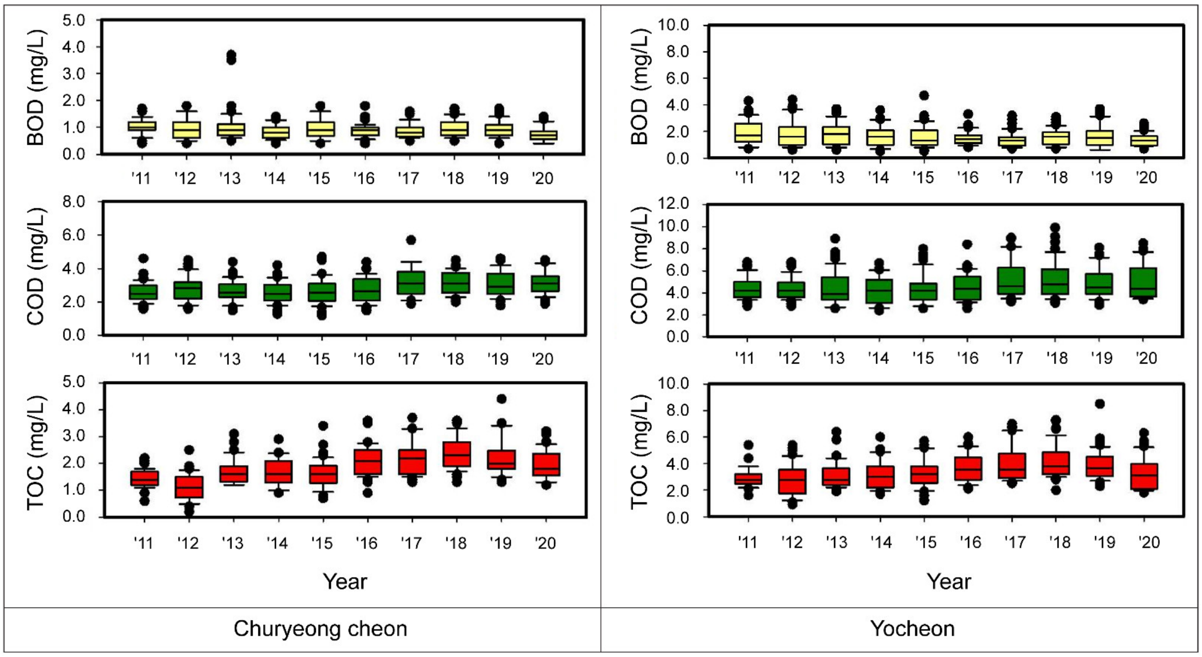

Figure 5. Annual average biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) at the measurement points.

The delivery load of a pollutant is the mass of a pollutant that passes a particular point of a river (such as a monitoring station on a watershed outlet) in a specified amount of time (e.g., daily, annually). Therefore, we estimated the pollutant loads of the studied parameters on a daily basis. Table 4 shows the observed water quality (BOD, COD, and TOC) and flow data during Phase 2 (2011–2015) and Phase 3 (2016–2020) of the TMDL management system. The minimum and maximum delivery loads of BOD, COD, and TOC in Churyeong A were observed in 2012 and 2017, respectively. BOD ranged from 56.765 to 23,467.450 kg/d, COD from 183.643 to 68,783.904 kg/d, and TOC from 144.089 to 32,368.896 kg/d.

Table 4. Annual average of delivery loads of pollutants (biological oxygen demand [BOD], chemical oxygen demand [COD], and total organic carbon [TOC]) at the measurement points.

Unit Basin	Item		'11	'12	'13	'14	'15	'16	'17	'18	'19	'20
Churyeon-gcheon	BOD (kg/d)	Min.	11.1	17.5	12.0	28.7	23.4	25.6	11.9	25.5	23.8	9.0
		Max.	1762.6	7196.4	652.5	1458.4	1271.0	1869.9	2231.7	2223.8	1863.5	1290.3
		Ave.	265.5	440.9	189.6	288.0	209.2	305.2	192.3	268.5	233.0	203.1
	COD (kg/d)	Min.	39.5	56.0	43.9	75.9	82.0	68.6	47.7	117.4	71.3	54.1
		Max.	5791.5	21,589.3	3508.9	5651.2	4267.1	7687.3	7381.7	8288.9	9317.7	8989.9
		Ave.	666.6	1526.4	635.0	960.5	579.6	1055.7	678.8	968.5	828.0	987.8
	TOC (kg/d)	Min.	22.1	21.0	31.1	35.9	41.0	58.3	33.8	84.0	58.8	27.1
		Max.	2769.8	11,994.0	2232.9	2916.7	3086.8	5817.5	4120.0	7278.0	7221.2	5288.2
		Ave.	365.9	674.6	398.0	609.0	355.0	802.4	469.4	735.3	636.5	648.8
Yocheon	BOD (kg/d)	Min.	174.1	160.6	198.9	144.6	92.9	225.5	56.8	168.9	158.6	183.8
		Max.	10,616.1	23,467.5	5515.2	7668.6	11,704.4	3441.0	2798.1	7172.3	3940.0	2603.1
		Ave.	1128.8	1612.3	1166.7	968.4	929.5	804.9	509.6	941.1	694.4	649.4
	COD (kg/d)	Min.	523.6	603.0	786.9	458.4	228.1	477.4	183.6	497.2	364.9	685.5
		Max.	31,184.9	68,783.9	12,894.5	26,163.5	30,344.6	16,146.4	11,192.4	19,842.9	11,006.4	10,021.8
		Ave.	2814.6	5120.7	3134.7	2829.6	2441.2	2523.3	2113.8	3297.1	2323.6	2524.8
	TOC (kg/d)	Min.	335.7	406.7	685.2	356.5	160.5	371.3	144.1	395.5	264.4	352.6
		Max.	18,578.2	32,368.9	7368.3	17,141.6	19,940.8	12,440.7	8394.3	17,008.2	11,549.9	6637.8
		Ave.	1792.4	2577.5	2168.4	2038.4	1747.0	2027.9	1591.9	2565.6	1948.4	1677.4

In Churyeong A, from 2011, BOD increased by 8.5% in 2014 and then decreased by 27.6% in 2020. COD increased by 44.1% from 2011 to 2014, 1.8% in 2017, and 48.2% in 2020. TOC increased by 66.5% from 2011 to 2014, 28.3% in 2017, and 77.3% in 2020 (Table 5 and Figure 6).

Table 5. Rate of change of delivery load of pollutants (kg/d) in Churyeong A and Yocheon B unit basins.

Unit Basin	Item	Delivery Load (kg/d)				Rate of Change (%)		
		'12 ①	'14 ②	'17 ③	'20 ④	Ratio (%) (②−①)/①∗100	Ratio (%) (③−①)/①∗100	Ratio (%) (④−①)/①∗100
Churyeon-gcheon	BOD	265.5	288.0	192.3	203.1	8.5%	−27.6%	−23.5%
	COD	666.6	960.5	678.8	987.8	44.1%	1.8%	48.2%
	TOC	365.9	609.0	469.4	648.8	66.5%	28.3%	77.3%
Yocheon	BOD	1128.8	968.4	509.6	649.4	−14.2%	−54.9%	−42.5%
	COD	2814.6	2829.6	2113.8	2524.8	0.5%	−24.9%	−10.3%
	TOC	1792.4	2038.4	1591.9	1677.4	13.7%	−11.2%	−6.4%

Numbers ①②③④ are representative values used in the calculation of the Rate of change.

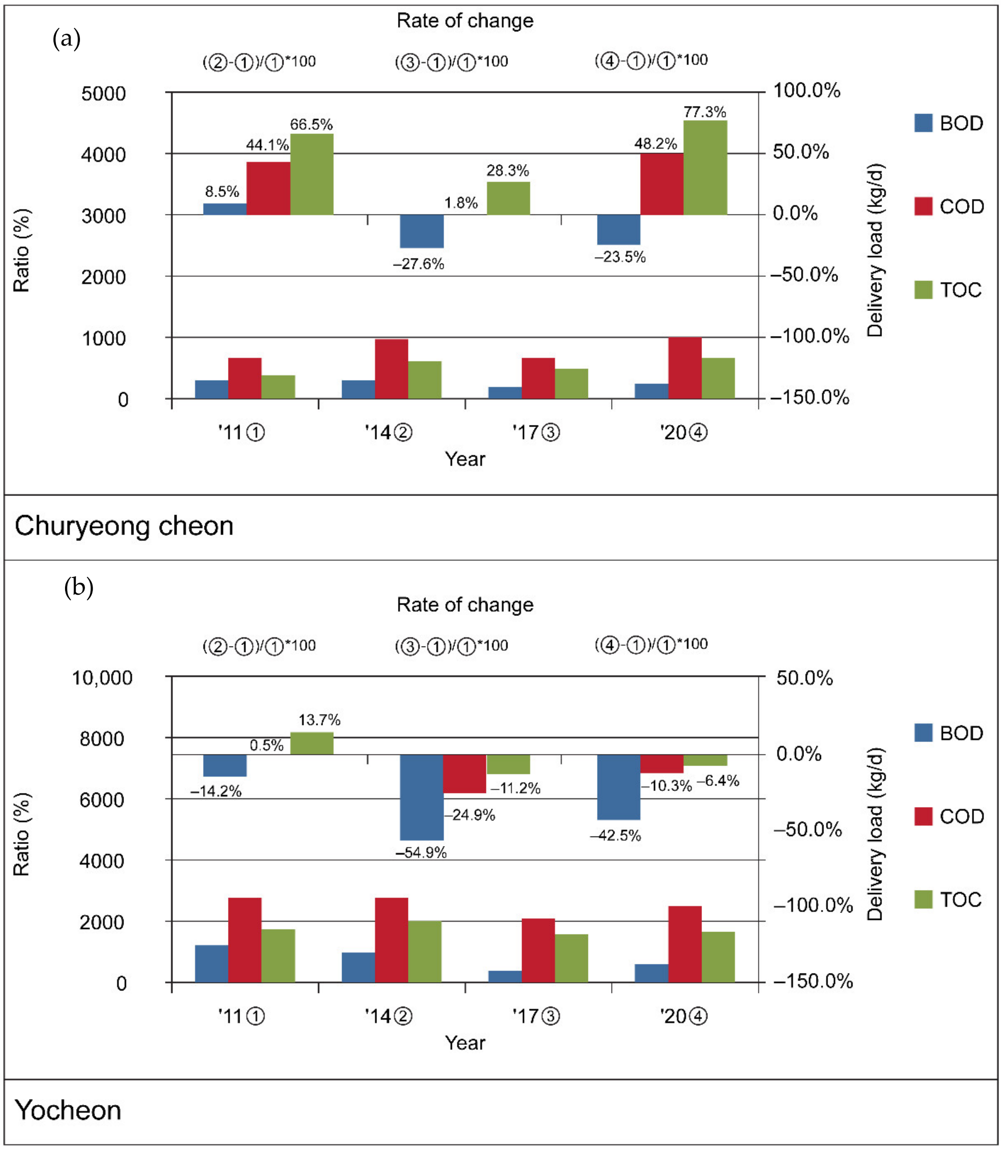

Figure 6. Rate of change of delivery loads of pollutants (kg/d) in (**a**) Churyeong A and (**b**) Yocheon B unit basins from 2011 to 2020. BOD: biological oxygen demand; COD: chemical oxygen demand; TOC: total organic carbon. Numbers ①②③④ are representative values used in the calculation of the Rate of change.

In Yocheon B, from 2011, BOD decreased by 14.2% in 2014, 54.9% in 2017, and 42.5% in 2020. Compared with the values in 2011, COD and TOC increased by 0.5% and 13.7% in 2014, respectively, and decreased in 2017 and 2020. Thus, BOD decreased in Churyeong A and Yocheon B, whereas COD and TOC increased in Churyeong A and decreased in Yocheon B, indicating different water quality change trends (Table 5 and Figure 6).

3.2. Water Quality Correlation Analysis

A correlation analysis was performed using the observed flow rate and water quality data to identify the water quality characteristics of the target basins. The assumptions of normality in the distribution of data, tested using the Kolmogorov-Smirnov test, were not satisfied ($p > 0.05$). However, regarding skewness and kurtosis of the descriptive statistics, the absolute values did not exceed 2.0 for all items except for SS, EC, and flow rate, indicating significance; therefore, the Pearson's correlation analysis was conducted (Tables 6 and 7).

Table 6. Normal distribution of measured data in Churyeongcheon.

Item	Kolmogorov–Smirnov	Descriptive Statistics		Standard Error
BOD (mg/L)	0	Skewness Kurtosis	0.64 0.05	0.12 0.24
pH	0	Skewness Kurtosis	−0.04 −0.21	0.12 0.24
DO (mg/L)	0	Skewness Kurtosis	0.33 −0.44	0.12 0.24
COD (mg/L)	0	Skewness Kurtosis	0.50 0.01	0.12 0.24
SS (mg/L)	0	Skewness Kurtosis	3.20 17.65	0.12 0.24
TN (mg/L)	0.003	Skewness Kurtosis	−0.19 −0.36	0.12 0.24
TP (mg/L)	0	Skewness Kurtosis	1.14 1.55	0.12 0.24
TOC (mg/L)	0	Skewness Kurtosis	0.66 0.72	0.12 0.24
EC (μS/cm)	0	Kurtosis Skewness	1.48 10.66	0.12 0.24
Flow rate (m^3/s)	0	Kurtosis Skewness	4.49 30.57	0.12 0.24

Table 7. Normal distribution of measured data in Yocheon.

Item	Kolmogorov–Smirnov	Descriptive Statistics		Standard Error
BOD (mg/L)	0	Skewness Kurtosis	1.06 0.91	0.12 0.23
pH	0.006	Skewness Kurtosis	−0.08 −0.15	0.12 0.23
DO (mg/L)	0	Skewness Kurtosis	0.17 −0.54	0.12 0.23
COD (mg/L)	0	Skewness Kurtosis	0.96 0.50	0.12 0.23
SS (mg/L)	0	Skewness Kurtosis	7.82 98.27	0.12 0.23
TN (mg/L)	0	Skewness Kurtosis	0.72 0.01	0.12 0.23
TP (mg/L)	0	Skewness Kurtosis	1.60 2.46	0.12 0.23
TOC (mg/L)	0	Skewness Kurtosis	0.86 1.05	0.12 0.23
EC (μS/cm)	0.054	Kurtosis Skewness	0.77 1.90	0.12 0.23
Flow rate (m^3/s)	0	Kurtosis Skewness	5.18 33.79	0.12 0.23

The correlation analysis focused on flow rate and organic matter (BOD, COD, and TOC). In Churyeong A, organic matter showed a strong significant correlation with TP and SS, and a negative correlation with DO. Flow rate showed a weak positive correlation with BOD (0.032) but a significant positive correlation with COD (0.252) and TOC (0.162)

(Table 8). This suggests that COD and TOC concentration, representing persistent organic matter, in Churyeong A, are greatly affected by runoff, such as sediment during rainfall, compared to BOD.

Table 8. Pearson correlation coefficient among the water quality parameters and flow rate in Churyeongcheon.

Items	pH	DO (mg/L)	BOD (mg/L)	COD (mg/L)	SS (mg/L)	TN (mg/L)	TP (mg/L)	TOC (mg/L)	EC (μS/cm)	Flow Rate (m^3/s)
pH	1									
DO (mg/L)	−0.024	1								
BOD (mg/L)	0.015	−0.2215 **	1							
COD (mg/L)	−0.043	−0.438 **	0.417 **	1						
SS (mg/L)	−0.143 **	−0.416 **	0.285 **	0.542 **	1					
TN (mg/L)	−0.164 **	0.178 **	0.078	−0.082	0.191 **	1				
TP (mg/L)	−0.132 **	−0.441 **	0.298 **	0.510 **	0.569 **	0.090	1			
TOC (mg/L)	0.012	−0.339 **	0.342 **	0.731 **	0.430 **	−0.163 **	0.451 **	1		
EC (μS/cm)	0.133 **	0.028	0.112 *	0.111 *	−0.031	−0.139 **	−0.018	0.210 **	1	
Flow rate (m^3/s)	−0.308 **	−0.199 **	0.032	0.252 **	0.493 **	0.339 **	0.423 **	0.162 **	−0.372 **	1

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed).

In Yocheon B, organic matter showed a strong significant correlation with TP and SS, and a negative correlation with DO; however, flow rate did not show a significant correlation with BOD, COD, or TOC (Table 9). This indicates that COD and TOC concentration in Yocheon B are not as greatly affected by nonpoint pollutant runoff during rainfall as those in Churyeong A, which can be attributed to the influence of the Namwon Sewage Treatment Plant.

Table 9. Pearson correlation coefficient among the water quality parameters and flow rate in Yocheon.

Item	pH	DO (mg/L)	BOD (mg/L)	COD (mg/L)	SS (mg/L)	TN (mg/L)	TP (mg/L)	TOC (mg/L)	EC (μS/cm)	Flow Rate (m^3/s)
pH	1									
DO (mg/L)	0.247 **	1								
BOD (mg/L)	0.055	−0.044	1							
COD (mg/L)	−0.103 *	−0.368 **	0.563 **	1						
SS (mg/L)	−0.112 *	−0.319 **	0.376 **	0.418 **	1					
TN (mg/L)	0.126 **	0.559 **	0.178 **	−0.154 **	−0.124 **	1				
TP (mg/L)	0.019	−0.263 **	0.509 **	0.494 **	0.418 **	−0.022	1			
TOC (mg/L L)	−0.071	−0.343 **	0.409 **	0.859 **	0.289 **	−0.192 **	0.381 **	1		
EC (μS/cm)	0.174 **	0.431 **	0.060	0.014	−0.276 **	0.573 **	-0.135 **	0.136 **	1	
Flow rate (m^3/s)	−0.305 **	−0.349 **	−0.057	0.057	0.523 **	−0.224 **	0.081	−0.054	−0.498 **	1

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed).

3.3. Seasonal Trend Analysis

For the application of the water quality evaluation method, basic data of the target basin and the characteristics of the observation point that influences the water quality evaluation were analyzed, and trends were analyzed through the regional/selective Mann–Kendall test.

Regional/seasonal Mann–Kendall test was used to analyze the trends of the water quality indexes. According to the results of the regional Kendall test for water quality items (BOD, COD, and TOC) of Churyeong A, the S statistics were −13, 52, and 45, respectively, at $p < 0.05$ (95% reliability), indicating significant trends of "no tendency," increasing," and "increasing," respectively. Data of Yocheon B were also analyzed, and BOD, COD, and TOC presented "no tendency," "no tendency," and "increasing" trends, respectively, with S statistics of −29, 17, and 40, respectively, at $p < 0.05$. This finding indicates an increase in concentrations of organic substances (Table 10).

Table 10. Seasonal Mann–Kendall/regional Kendall test results with biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).

Measurement Point	Item	Seasonal Mann–Kendall Trend					
		Statistic S	Z	p	Kendall's Tau	Slope (mg/L/y)	Trend
Churyeong A	BOD	−13	−0.774	0.439	−0.144	0.924	▬
	COD	52	3.269	0.001	0.578	2.458	▲
	TOC	45	2.800	0.005	0.500	1.275	▲
Yocheon B	BOD	−29	−1.789	0.074	−0.322	1.719	▬
	COD	17	1.024	0.306	0.189	4.075	▬
	TOC	40	2.477	0.013	0.444	2.675	▲

▲ upward trend, ▼ decreasing trend, ▬ no trend change.

3.4. Model Evaluation Method

NSE, PBIAS, and RSR were used to evaluate the load simulated by the regression model. In this study, we applied the monthly simulation values proposed by Moriasi et al. to evaluate a model fit for statistical variance [14]. The index is primarily used to evaluate the quantitative reliability of the model-calculated values and observed values, and consists of four ratings: very good, good, satisfactory, and unsatisfactory.

According to Moriasi et al., the simulation results of monthly runoff data are satisfactory when NSE is 0.50 or more and RSR is 0.70 or less [14]. Engel et al., reported that generally, the statistical variance of model simulation results decreases with shorter time intervals [15].

In Churyeong A, BOD, COD, and TOC were rated as "very good" (Table 11), indicating that the calculated values using the LOADEST model had high reliability. Figure 7 shows a comparison between the observed loads and simulated loads using the regression model, in which the statistical variance was lower than the observed values for load (Figures 7 and 8). In Figures 7 and 9, the simulated value is the value calculated using the LOADEST model.

Table 11. Evaluation according to the general performance rating for recommended statistics for Churyeong A and Yocheon B.

Unit Basin	Item	NSE		PBIAS (%)		RSR	
Churyeong A	BOD	0.92	Very good	0.53	Very good	0.29	Very good
	COD	0.96	Very good	−0.15	Very good	0.19	Very good
	TOC	0.94	Very good	−0.81	Very good	0.24	Very good
Yocheon B	BOD	0.83	Very good	0.49	Very good	0.46	Very good
	COD	0.91	Very good	0.99	Very good	0.33	Very good
	TOC	0.91	Very good	1.25	Very good	0.34	Very good

The metrics for Yocheon B were rated as "very good" (Table 11), indicating that the regression model reflected the observations well. The observed values for load were compared with the calculated values on a scatter plot, which showed that the statistical variance was lower than that of the observed values; however, it was considered to be suitable for simulating pollutant loads and identifying trends (Figures 9 and 10).

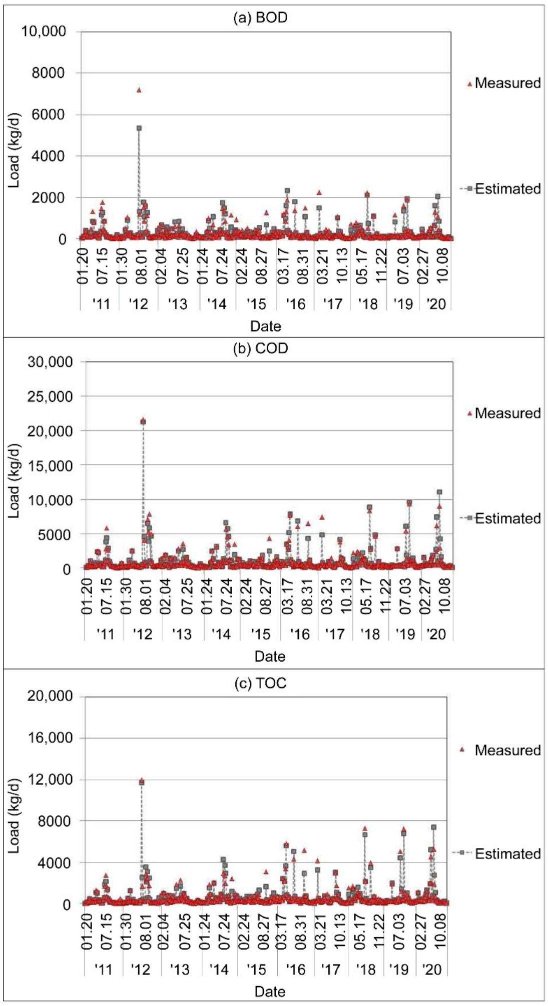

Figure 7. Comparison of the calculated (**a**) biological oxygen demand (BOD), (**b**) chemical oxygen demand (COD), and (**c**) total organic carbon (TOC) loads and the LOADEST loads in Churyeongcheon.

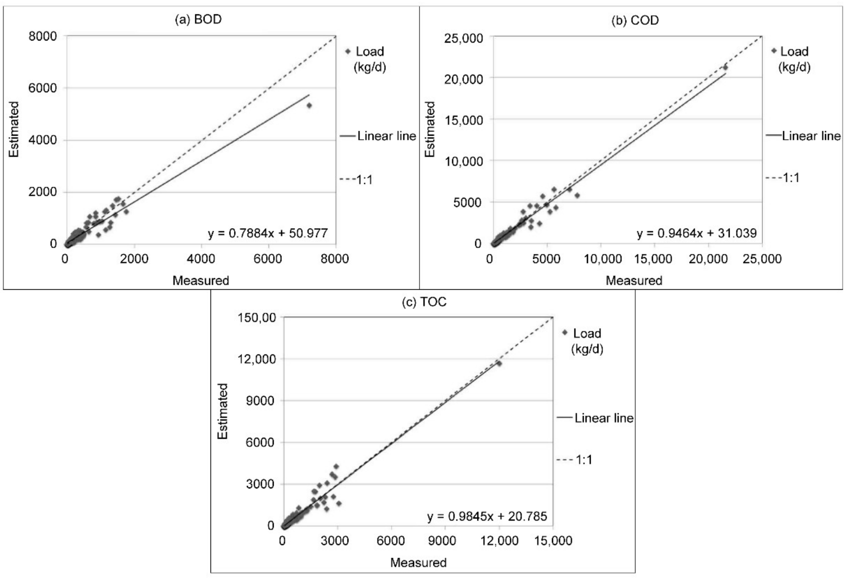

Figure 8. Comparison of (**a**) BOD, (**b**) COD, and (**c**) TOC loads and LOADEST loads in Churyeongcheon.

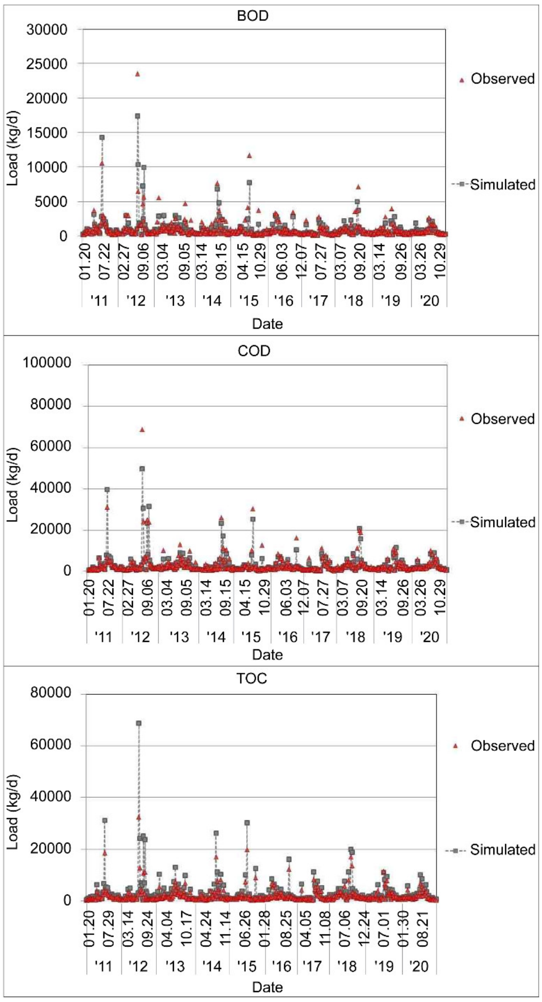

Figure 9. Comparison of water quality item load and maximum load calculated for Yocheon.

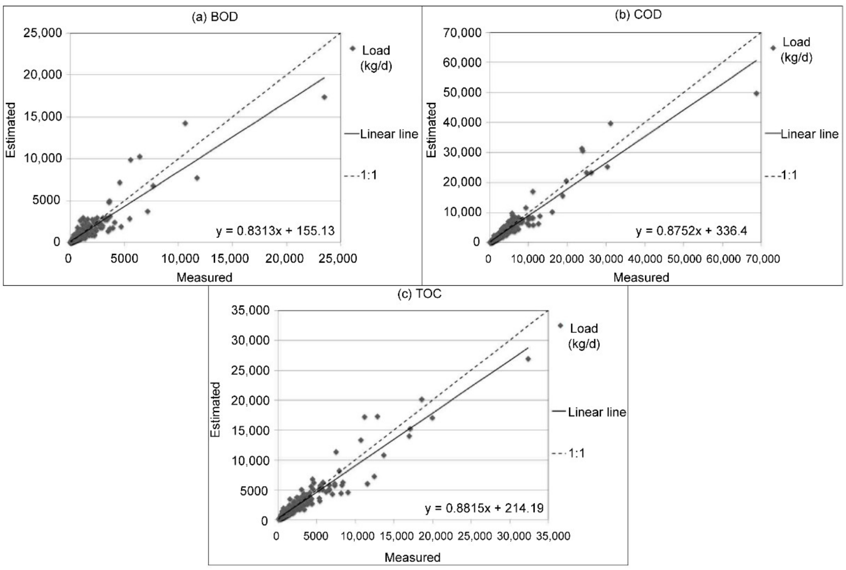

Figure 10. Comparison of water quality item load and maximum load calculated for Yocheon.

3.5. Regression Analysis of the LOADEST Model

The LOADEST model uses maximum likelihood estimation (MLE), adjusted maximum likelihood estimation (AMLE), and least absolute deviation (LAD) to estimate parameters of the regression equation. MLE and AMLE are used when the corrected model residuals follow a normal distribution, and LAD is used when they do not. When to use MLE or AMLE is determined based on whether the outliers of flow rate or water quality data used in model calibration are corrected; AMLE is used if they are adjusted, and MLE if they are not [16]. The parameters of the regression equation applied to the AMLE method were analyzed to investigate trends in BOD, COD, and TOC at the target measurement points.

3.5.1. Trend Analysis for Churyeongcheon

The regression coefficient α1, indicating the flow rate dependence of BOD in Churyeong A, was statistically significant, indicating that the load increased as the flow rate increased. The time regression coefficient, α5, was statistically significant at −0.0107 and indicated a decrease over time (Table 12).

Table 12. Values of the adjusted maximum likelihood estimation (AMLE) variable of the calculated LOADEST model in Churyeongcheon.

Item	α0	α1	α2	α3	α4	α5	α6	R^2
BOD	5.1020 **	0.9642 **	0.0180 *	0.0923 **	−0.2386 **	−0.0107 *	−0.0014	93.15
COD	6.2301 **	1.0011 **	0.0335 **	0.0380 **	−0.2514 **	0.0244 **	0.0024 *	97.50
TOC	5.8323 **	0.9882 **	0.0362 **	−0.0468 **	−0.3228 **	0.0667 **	−0.0080 **	95.00

**: highly significant, *: significant.

The regression coefficient α1 for COD and TOC was also a statistically significant positive value and exhibited a high correlation with flow rate (Table 12). The time regression coefficient α5 indicated a statistically significant increasing trend for both COD and TOC. Therefore, in Churyeong A, BOD exhibited a statistically significant decreasing trend, whereas COD and TOC, which represent persistent organic matter, exhibited increasing trends (Table 13).

Table 13. Adjusted maximum likelihood estimation (AMLE) regression statistics in Churyeongcheon.

Item		α0	α1	α2	α3	α4	α5	α6
BOD	Std. Dev.	0.0236	0.0141	0.0100	0.0202	0.0212	0.0050	0.0019
	T-ratio	216.52	68.26	1.79	4.56	−11.27	−2.15	−0.73
	p	<0.01	<0.01	>0.01	<0.01	<0.01	>0.01	>0.1
COD	Std. Dev.	0.0143	0.0086	0.0061	0.0123	0.0129	0.0030	0.0012
	T-ratio	434.60	116.49	5.48	−3.08	−19.53	8.05	2.01
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	>0.01
TOC	Std. Dev.	0.0209	0.0125	0.0089	0.0180	0.0188	0.0044	0.0017
	T-ratio	278.67	78.77	4.05	−2.60	−17.17	15.06	−4.68
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

3.5.2. Trend Analysis for Yocheon

The *p*-value of the BOD regression coefficient in Yocheon B showed high significance for α1–5, whereas α6 showed no significance (Table 13). For BOD, the parameter of the regression coefficient α1 was positive, indicating that it was affected by increased flow rate, whereas the time regression coefficient α5 was negative, indicating that BOD decreased over time. For COD, the regression coefficients α0–5 showed high significance and α6 showed moderate significance. For TOC, α0, α1, and α3–6 showed high significance and α2 showed moderate significance. The parameters of α1 for COD and TOC were 0.9686 and 0.9204, respectively, indicating that they increased with an increase in flow rate. Both COD and TOC exhibited a statistically significant increase in change over time, and increased in winter (Tables 14 and 15).

Table 14. Values of the adjusted maximum likelihood estimation (AMLE) variable of the calculated LOADEST model in Yocheon.

Item	α0	α1	α2	α3	α4	α5	α6	R^2
BOD	6.5426 **	0.9739 **	0.0422 **	0.3826 **	−0.0804 **	−0.0215 **	0.0036	84.08
COD	7.6773 **	0.9686 **	0.0347 **	0.1597 **	−0.2240 **	0.0185 **	0.0033 *	94.41
TOC	7.4094 **	0.9204 **	0.0227 *	0.1459 **	−0.2604 **	0.0377 **	−0.0052 **	91.25

**: highly significant, *: significant.

Table 15. Adjusted maximum likelihood estimation (AMLE) regression statistics for Yocheon.

Item		α0	α1	α2	α3	α4	α5	α6
BOD	Std. Dev.	0.0278	0.0224	0.0150	0.0242	0.0255	0.0057	0.0022
	T-ratio	234.97	43.38	2.81	15.83	−3.15	−3.75	1.58
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	>0.1
COD	Std. Dev.	0.0162	0.0131	0.0087	0.0140	0.0148	0.0033	0.0013
	T-ratio	474.22	74.21	3.97	11.37	−15.10	5.54	2.49
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	>0.01
TOC	Std. Dev.	0.0199	0.0161	0.0107	0.0173	0.0183	0.0041	0.0016
	T-ratio	371.69	57.27	2.12	8.43	−14.25	9.18	−3.21
	p	<0.01	<0.01	>0.0 1	<0.01	<0.01	<0.01	<0.01

4. Discussion

To analyze water quality trends in the Churyeongcheon and Yocheon TMDL unit basins of the Seomjin River system, we examined the correlations of long-term observation data and water quality trends using a regression equation of the LOADEST model.

The Churyeong A unit basin has a high proportion of nonpoint sources compared to point sources. The increase in organic matter in the unit basin was found to be related to the flow rate and was affected by nonpoint sources that flow into the river during rainfall, an external factor. In Yocheon B, variations in water quality showed little relation to flow rate or unit basins with a high proportion of nonpoint sources that correlated with point sources.

To analyze the water quality index trends, the regional/seasonal Mann–Kendall test was performed. In Churyeong A, TOC showed a tendency to "increase." Similarly, in Yocheon B, TOC tended to "increase," and organic matter increased in the target basins.

The loads of organic matter were simulated based on the loads of organic matter in the target basins using observation data and a regression equation of the LOADEST model. The results showed that organic matter (BOD, COD, and TOC) in Churyeong A exhibited seasonality under the influence of an increase in flow rate. BOD load decreased over time, whereas COD and TOC increased over time. In Yocheon B, organic matter trends were affected by increased flow rate. BOD decreased over time, and COD and TOC increased over time and exhibited seasonality.

In Churyeong A and Yocheon B, BOD decreased, whereas TOC, which is measured based on the total amount of organic matter, increased. Particularly, in Churyeong A, which had a high proportion of plants, the source of humus was influenced by external inflows. Accordingly, future research should identify the origins and characteristics of organic matter.

Nevertheless, the influencing factors and trends of organic matter based on long-term observation data presented herein could facilitate the formulation of appropriate water quality management policies.

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