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Investigating the applicability and assumptions of the regression relationship between flow discharge and nitrogen concentrations for load estimation

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ABSTRACT

The regression relationship between water discharge rates and nutrient concentrations can provide a quick and straightforward way to estimate nutrient loads. However, recent studies indicated that the relationship might produce large biases in load estimates and, therefore, may not be applicable in certain types of cases. The goal of this study is to explore the theoretical reasons behind the selective applicability of the regression relationship between flow rates and nitrate + nitrite concentrations. For this study, we examined daily flow and nitrate + nitrite concentration observations made at the outlets of 22 watersheds monitored by the Heidelberg Tributary Loading Program (HTLP). The statistical relationship between the flow rates and concentrations was explored using regression equations offered by the LOAD ESTimator (LOADEST). Results demonstrated that the use of the regression equations provided nitrate + nitrite load estimates at acceptable accuracy levels ($NSE \geq 0.35$ and $|PBIAS| \leq 30.0\%$) in 14 watersheds (64 % of 22 study watersheds). The regression relationships provided highly biased results at eight watersheds (36 %), implying their limited applicability. The heteroscedasticity of the residuals led to the high bias and resulting inaccurate regression, which was commonly found in watersheds where low flow had high nitrate + nitrite concentration variations. Conversely, the regression relationships provided acceptable accuracy for watersheds that had a relatively constant variance of the nitrate + nitrite concentrations. The results indicate that the homoscedasticity of residuals is the key assumption to be satisfied to estimate nitrate + nitrite loads from a statistical regression between flow discharge and nitrate + nitrite concentrations. The transport capacity (capacity-limited) concept implicitly assumed in the regression relationship between flow discharge and nitrate + nitrite concentrations is not always applicable, especially to agricultural areas in which nitrate + nitrite loads are highly variable depending on management practices (supply-limited). The

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findings suggest that the regression relationship should be carefully applied to areas in which intensive agricultural activities, including crop management and conservation practices, are implemented. Thus, the transport capacity concept is reasonably regarded to contribute to the homoscedasticity of residuals.

1. Introduction

Accurate nutrient load estimates are critical to developing water quality management plans [1–3]. The load estimation is also required when evaluating the health and safety of water consumption [4], maintaining ecological balance [5], and mitigating challenges posed by changing climatic conditions [6]. Monitoring and modeling approaches have helped estimate nutrient loads to downstream waterbodies from upstream watersheds and associated streams [1,7]. Monitoring provides field observations required to describe and assess the water quality conditions based on pollution indices [8–10], but they are often too expensive to conduct, especially at large spatial and fine temporal scales [3,11]. The use of mechanistic models can be an efficient way to quantify the amount of nutrient load to downstream waterbodies [12]. Since such models usually need a significant amount of data to represent the landscape and require the calibration of many equations and parameters, uncertainty in the modeling results is always of concern [13, 14]. For example, Her and Chaubey [13] demonstrated that both output and parameter uncertainty in mechanistic models are responsive to the number of observations and calibration parameters. Similarly, Shrestha et al. [14] indicated that additional calibration at multiple locations does not always improve the accuracy of mechanistic modeling. When there is insufficient information about the watershed features and parameters to prepare a mechanistic model, statistical models can be a quick but still reliable tool to quantify nutrient loadings [15–17].

The regression relationship between flow discharge rates and nutrient loads has been commonly used to estimate the amount of nutrient carried by flowing water [16,18,19]. The literature revealed large variations in the estimation accuracy provided by the regression relationships, depending on the water quality constituents, sampling sites, and sampling regimes [15,16,20]. For example, Hirsch [16] noted that the lack of fit in the relationship between concentration and discharge, substantial differences in this relationship across seasons, and pronounced heteroscedastic residuals are primary factors leading to estimate biases. Additionally, Lee et al. [16] observed that sampling record characteristics—including sampling strategy, length, and frequency—substantially influence the accuracy of load estimates. Verma et al. [21] reported that regression equations might not accurately estimate nitrate loads with short monitoring durations and low frequencies. On the other hand, Esralew et al. [22], Carey et al. [23], and Park and Engel [24] demonstrated that the regression relationship could provide acceptable accuracy of nitrate + nitrite and sediment load estimates, especially in areas where agricultural land uses are relatively small.

LOADEST is a statistical modeling tool developed to estimate constituent loads from flowing water in streams and rivers [25]. It requires only streamflow data and water quality concentration measurements. Based on this information, LOADEST identifies a regression equation that can describe the relationship between constituent loads and flow discharge measurements. This equation is then used to estimate constituent loads for unmeasured periods across various temporal scales [25]. LOADEST has been widely employed not only to quantify various constituent loadings to watershed outlets but also to create reference data sets for calibrating hydrological model parameters [26–29].

As a statistical model, however, LOADEST does not consider a causal relationship but only a correlation between flow and concentration, and, thus, it does not explain the mechanism of how runoff carries nutrients [15,30]. The statistical tests implemented by LOADEST do not consider potential errors in the observations; therefore, the statistical confidence is likely to be overestimated [31]. The statistical analysis using LOADEST assumes the steady state of a watershed and stream system of interest, which means there should be no long-term trend in the data. It also assumes the homoscedasticity, normality, and independence of the data (or residuals) [25]. Hirsch [15] demonstrated that assumptions of homoscedasticity of model errors and fixed relationships between concentration and each covariate in LOADEST can lead to severe bias in constituent loads estimations. This result corroborates Stenback et al. [19], who demonstrated that the poor performance of LOADEST was associated with residual heteroscedasticity.

Studies demonstrated that the consideration of temporal variations in the relationships between flow rates and concentrations could improve the accuracy of load estimation [15,30]. For example, generalized additive models (GAMs), such as the loads regression estimator, incorporate smoothing functions for the covariates [1]. Unlike LOADEST, which uses predefined forms based on relationships—such as linear, quadratic, and logarithmic between discharge and water quality concentration—GAMs do not adhere to a fixed form. They are not necessarily linear, and they strive to capture the primary characteristics of the data [32]. This inherent flexibility in the GAM approach enables it to handle multiple nonlinear functional responses [1]. The weighted regressions on time, discharge, and season (WRTDS) take into account differences across times (or days), seasons, and flow discharges [33]. They assign heavier weights to observations that are more relevant (or closer) to specific estimation points (or dates) in the regression [30]. In contrast, LOADEST uses fixed relationships among time, discharge, and concentrations. Hirsch [15] reported that WRTDS could more precisely represent the temporal variations of water quality patterns and, thus, produce more accurate load estimates than LOADEST.

However, Lee et al. [16] found that the accuracy of statistical load estimation methods, including LOADEST and WRTDS, was dependent on the types of water quality variables, areas, and sampling frequencies, and there was no single model that could always provide the most accurate estimates. In addition, the estimates of WRTDS are sensitive to the value selection of parameters, "half-window widths" for the weights of long-term, seasonal trends and discharge [33]. No known studies have evaluated the potential impacts of weight function selection (i.e., "tricube weight function") and weight integration method (i.e., "the product of the three component weights") on the accuracy of WRTDS. Furthermore, the flexibility in GAM heightens the risk of overfitting when the model becomes too specialized to the training data. While linear models have intuitive coefficients, the smoothing functions in GAM introduce nonlinear relationships, complicating the interpretation of coefficients [34]. The sound yet simple statistical procedures of LOADEST made it useful in many applications until recently [26,35–38].

Previous studies revisited statistical relationships or evaluated sampling strategies to understand how biases and errors could be introduced into nitrate + nitrite load estimates [3,15,16,21]. However, they did not address assumptions and the resulting inherent limitations of a regression relationship to be constructed between flow rates and nutrient loads. In addition, it is still unclear which characteristics of watersheds make the regression relationship unsuitable to them. Further explorations are needed regarding the fundamental reasons that might render the regression relationship inapplicable in certain cases. This study did not attempt to simply criticize the regression models but sought to address the questions.

The objective of this study is to explore the theoretical reasons why the applicability of the regression relationship between flow rates and nitrate + nitrite concentrations is selective. To answer this question, we investigated the performance of the regression relationships constructed by using daily flow rates and nitrate + nitrite concentrations observed in 22 study watersheds with varying land uses and covers, as described in the Materials and Methods section. The accuracy of the regression relationships was assessed quantitatively, and the residuals were investigated in the Results section. Then, in the Discussion section, we explored what made the regression models applicable or inapplicable to certain cases with consideration of sampling strategies, watershed characteristics, and nutrient transport theories.

2. Materials and methods

2.1. Regression model

2.1.1. LOADEST

In this study, we employed LOADEST to explore the applicability of the regression relationship between flow discharge and nutrient concentrations. LOADEST is a statistical modeling tool designed to estimate constituent loads in flowing water from streams and rivers [25] and includes nine regression models (Table 1). In these models, streamflow and decimal time are used as independent variables to predict pollutant loads, which are the dependent variables [25]. As a statistical model, LOADEST's assumptions include homoscedasticity, normality, and independence of the data or residuals (Runkel et al., 2004). Furthermore, the model assumes that the relationships among concentration, discharge, and time (as outlined in Table 1) are predefined and remain constant over time. LOADEST has been widely used to estimate comprehensive records of daily concentrations and daily constituent loads from complete daily discharges. These predictions are often used as calibration data for mechanistic models [26–29]. A more in-depth background and theory related to LOADEST can be found in Runkel et al. [25].

2.1.2. Model calibration

The coefficients of the predefined regression models (Table 1) were calibrated using the adjusted maximum likelihood estimation (AMLE), which is the primary load estimation method used within LOADEST [25,39]. The model coefficients in regression equations are estimated by maximum likelihood estimates that are corrected for first-order bias [25]. AMLE assumes that the calibration model error (or residuals) follows a normal distribution and allows for the use of water quality data sets containing censored data [40]. Cohn [41] demonstrated that AMLE exhibits negligible bias and performs better than any of the alternative estimators tested. More detailed procedures for estimating the model coefficients in regression equations using AMLE can be found in Cohn [41].

2.1.3. Model selection

A regression model is selected from candidate regression models 1–9 (Table 1) based on the Akaike information criterion (AIC)

Table 1
Regression models in the LOADEST.

Model number	Regression model
1	$\ln(Load) = a_0 + a_1 \ln\widehat{Q}$
2	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 \ln \widehat{Q}^2$
3	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 dtime$
4	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2\, sin(2\pi dtime) + a_3\, cos(2\pi dtime)$
5	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 \ln \widehat{Q}^2 + a_3 dtime$
6	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 \ln \widehat{Q}^2 + a_3\, sin(2\pi dtime) + a_4\, cos(2\pi dtime)$
7	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2\, sin(2\pi dtime) + a_3\, cos(2\pi dtime) + a_4 dtime$
8	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 \ln \widehat{Q}^2 + a_3\, sin(2\pi dtime) + a_4\, cos(2\pi dtime) + a_5 dtime$
9	$\ln(Load) = a_0 + a_1 \ln\widehat{Q} + a_2 \ln \widehat{Q}^2 + a_3\, sin(2\pi dtime) + a_4\, cos(2\pi dtime) + a_5 dtime + a_6 dtime^2$

Note: $\ln Q$ = ln(streamflow), $\ln\widehat{Q}$ = ln(streamflow) – center of ln(streamflow); *dtime* = decimal time – center of decimal time; the center of data $T = \overline{T} + \frac{\sum(T-\overline{T})^3}{2\sum(T-\overline{T})^2}$, and $\overline{T}$ = the mean of the data T [25].

[25]. The AIC is a mathematical formula used for model selection and for evaluating efficiency in terms of model structure. The formula for this criterion is presented as (Equation (1)):

$$AIC = -2\ln\left(\sigma_{\epsilon}^{2}\right) + 2k \tag{1}$$

where σ_{ϵ}^{2} denotes the maximum likelihood estimate of the residuals' variance and k is the number of parameters. The term $2k$ serves as a penalty to prevent the formula from leaning toward a model with an excessive number of parameters [42]. Typically, a model with a smaller AIC value suggests a better predictive performance. Thus, the model with the lowest value of the AIC statistic is selected for use in load estimation. Accordingly, the selected model is used to construct a complete time series of nutrient concentrations and, then, loads by multiplying the concentrations by the corresponding discharge. More detailed procedures for selecting regression models using AIC can be found in Bonakdari and Zeynoddin [42].

2.2. Assessment criteria

Nitrate + nitrite loads estimated using the regression relationships (or LOADEST) were compared with field measurements obtained by multiplying observed daily nitrate + nitrite concentrations by observed daily flow discharge to evaluate the accuracy of the estimates.

Three statistics were employed to quantify the accuracy (Equations (2)–(4)):

$$R^2 = \left[\frac{\sum_{i=1}^{n}(O_i - \overline{O})(P_i - \overline{P})}{\sqrt{\sum_{i=1}^{n}(O_i - \overline{O})^2}\sqrt{\sum_{i=1}^{n}(P_i - \overline{P})^2}}\right]^2 \tag{2}$$

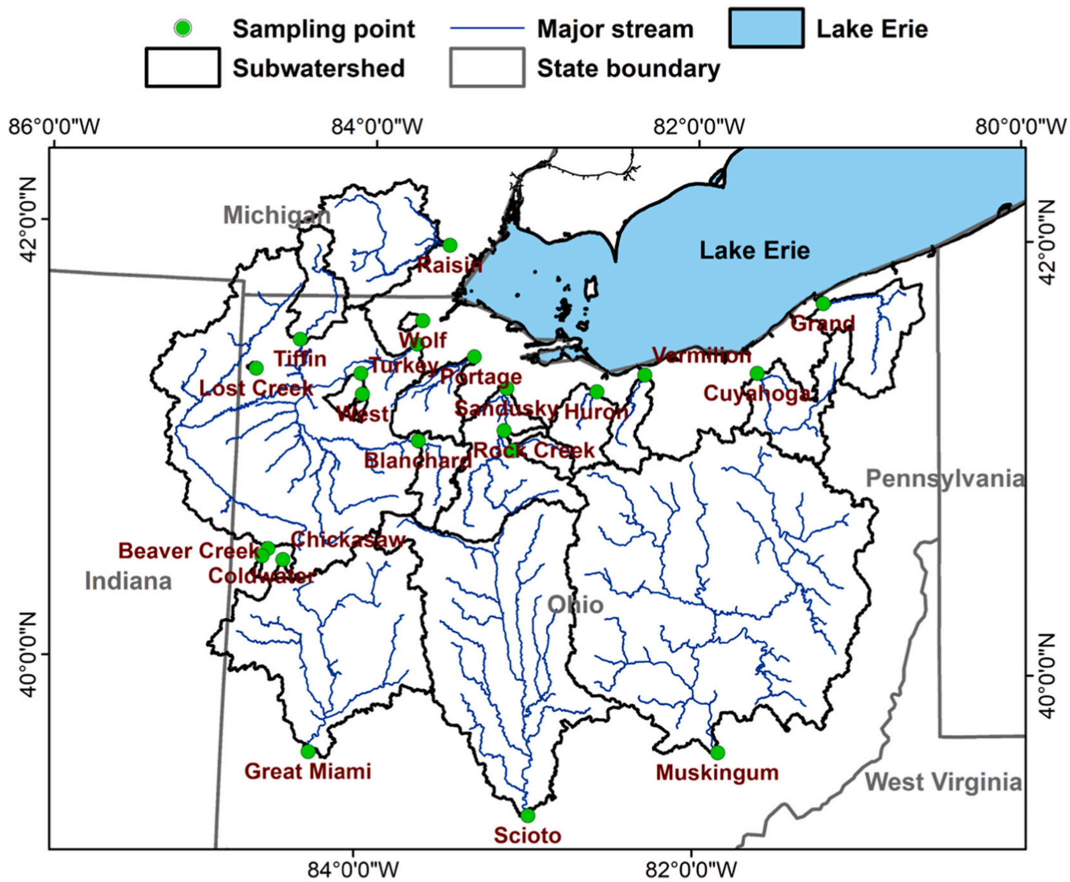

Fig. 1. Locations of the National Center for Water Quality Research water quality monitoring sites and associated watersheds draining water and nutrients to Lake Erie [51].

$$NSE = 1 - \left[\frac{\sum_{i=1}^{n} (O_i - P_i)^2}{\sum_{i=1}^{n} (O_i - \overline{O})^2} \right] \tag{3}$$

$$PBIAS = \frac{\sum_{i=1}^{n} (O_i - P_i)}{\sum_{i=1}^{n} O_i} \tag{4}$$

where O and P represent the observed and simulated loads (kg/day), respectively; n is the number of time steps at a time step i; and the over-bar represents an average of the given variable over the selected period. R^2 estimates the combined dispersion relative to the single dispersion of both the observed and predicted series. A value of zero indicates no correlation, while a value of 1 signifies that the dispersion of the prediction equals that of the observation [43]. NSE [44] is effective for use with continuous long-term simulations, and it can be used to assess how accurately the model simulates trends for the concerned output response [45]. The NSE ranges between 1.0 (indicating a perfect fit) and -∞. The percent bias ($PBIAS$) was used to evaluate the overall relative discrepancy between observed and estimated loads [46]. This study employed performance criteria recommended to differentiate between "satisfactory" and "unsatisfactory" performance by Moriasi et al. [45]: $NSE \geq 0.35$ and $|PBIAS| \leq 30.0\%$.

2.3. Study areas and data

This study focused on the HTLP stations at which daily nitrate + nitrite concentration and flow discharge records were made at the outlets of 22 watersheds. These records were available from the National Center for Water Quality Research (NCWQR; https://ncwqr-data.org/HTLP/Portal) at Heidelberg University, OH, USA [2,47–51] (Table 1, Figs. 1 and 2). The HTLP stations were selected because the nitrate + nitrite concentration observations had undergone rigorous quality control in adherence to the standards set forth by the NCWQR. Water samples were analyzed using accepted U.S. Environmental Protection Agency analytical methods at NCWQR laboratories [3]. Furthermore, each HTLP station is partnered with U.S. Geological Survey (USGS) flow discharge gauging stations. Stream flow is quantified as daily flow discharge, which is a daily mean discharge value determined from high-frequency (typically 15-min interval) water level measurements. This is combined with USGS protocols for using stage-discharge relationships that depend on much less frequent direct discharge measurements [52]. Daily nutrient concentrations can be converted to daily loads by multiplying the concentrations by the corresponding daily flow discharges. Such detailed (daily) and long-term flow and water quality records served as the reference data to be compared with load estimates made using the regression relationship for their accuracy assessment. As of July 2020, all available data were used for estimating nitrate + nitrite loads from streamflow discharge and time in this study. The daily streamflow discharge and nitrate + nitrite concentration observations were fed into LOADEST to explore the regression equations.

The study watersheds are located in the Corn Belt, a region of the Midwestern United States that is vital for providing land resources for food and energy production, mainly with corn and soybeans. The crop productivity has been enhanced by applying fertilizers (e.g., urea and diammonium phosphate) and using conservation practices (e.g., crop rotations and cover crops) in the Corn Belt [28,53]. Because of the poorly drained soils in this region, tile drainage systems are extensively used to efficiently remove excess water from the soil [54,55]. Despite some watersheds being nested within larger ones, individual watersheds can indeed possess distinct hydrological characteristics. The 22 study watersheds have various drainage areas from 11 km^2 to 19,215 km^2, with a variety of land uses and

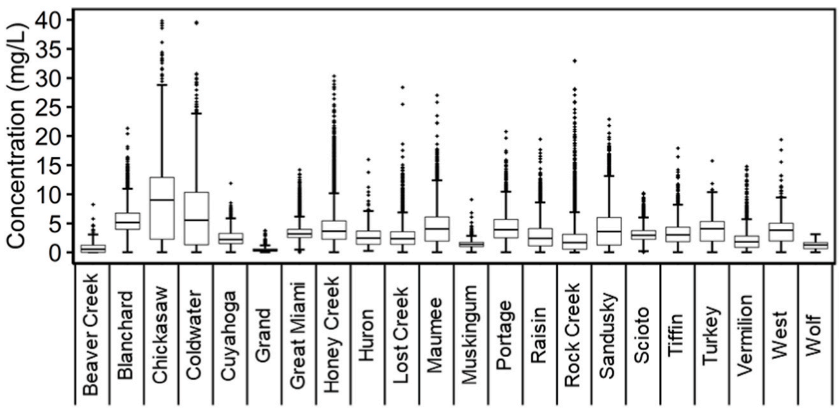

Fig. 2. Comparison between the distributions of daily nitrate + nitrite concentrations from the 22 stations. In the box plot, the height represents the interquartile range (between the 75th and 25th percentiles), and the line that divides the box into two parts indicates the median. The ends of the whiskers signify the maximum and minimum values. This figure was drawn using the Heidelberg Tributary Loading Program data [51], which were monitored by the National Center for Water Quality Research.

topography: agriculture (9.0%–92.3 %) and forest (0.9%–48.1 %) and drainage densities from 0.18 to 0.69 km^{-1} (Table 2). These differences in the hydrological characteristics can lead to variations in nutrient discharge patterns among the watersheds [2]. Across the study watersheds in the Corn Belt regions, annual precipitation ranges between 833 mm/year and 1135 mm/year. Typically, 55 % of the year's total precipitation falls between March and July [56].

3. Results

3.1. Accuracy assessment

Various regression equations were selected based on the lowest AIC values (Table 3). AIC assesses the model fit in relation to the number of explanatory variables and penalizes models with excessive variables (refer to Equation (1)). The model with the lowest AIC is considered the most parsimonious [57]. Consequently, Model 9 was the most frequently selected, chosen for 19 stations (86 %). Model 8 was selected for two stations (9 %), and Model 6 for one station (5 %).

The coefficients of the selected regression models were determined using AMLE (Table 4). For the 22 watersheds, the R^2 values of the regression equations, as indicated in Table 4, ranged from 0.62 to 0.94. While the number of coefficients varies among Models 6, 8, and 9, the independent variables remain consistent as streamflow and decimal time across all models.

The regression relationship identified by applying LOADEST to total runoff provided the nitrate + nitrite load estimates with "satisfactory" accuracy statistics at 64 % (14 of 22) of the monitoring stations (Fig. 3). The regression relationship also provided highly biased results at 36 % (eight of 22) of the stations. In the 'satisfactory' case, the overall simulated results demonstrated a good fit with the observations (Fig. 4(a)). In the "unsatisfactory" cases, the regression overestimated the upper ranges of the load estimates, which led to large biases in the load estimates. For example, the regression relationship failed to capture the peak loads in the Maumee watershed: On June 14, 1998, the observed value was 430,600 kg/day, whereas the simulated value was 1,031,700 kg/day (240 %); see Fig. 4(b). Additionally, the regression relationship overestimated the total loads (*PBIAS* of 58 %); see Fig. 3. As a result, the regression relationship consistently overestimated nitrate + nitrite loads when compared to the observations at daily, monthly, and annual scales in the "unsatisfactory" cases (Fig. 5(b)). In Fig. 5(a), for the Muskingum watershed (the "satisfactory" case), the points on

Table 2
National Center for Water Quality Research water quality monitoring periods and the watershed characteristics (NCWQR: https://ncwqr-data.org/HTLP/Portal).

Watershed	Drainage Area (km^2)	Data Period Used		Agriculture (%)	Pasture (%)	Forest (%)	Urban (%)	Other (%)	PDSC[a] (%)	DD[b] (km^{-1})
		Begin	End							
Beaver Creek	294	11/11/13	12/19/16	69.1	7.3	2.4	1.6	18.7	67.7	0.28
Blanchard	896	9/3/07	7/4/20	78.8	3.5	6.3	10.5	1.0	84.5	0.27
Chickasaw	43	10/24/08	7/4/20	79.0	8.9	2.8	9.1	0.1	75.9	0.50
Coldwater	30	10/15/12	7/1/20	68.8	14.0	2.6	12.2	2.5	79.6	0.43
Cuyahoga	1830	11/4/81	3/15/20	9.0	11.8	33.6	39.5	6.1	38.0	0.28
Grand	1774	3/1/88	8/10/06	40.0	-*	50.1	0.9	13.1	82.6	0.42
Great Miami	7019	4/22/96	7/4/20	64.5	8.5	8.6	17.0	1.4	54.6	0.33
Honey Creek	386	1/28/76	7/4/20	81.1	2.0	9.5	6.7	0.7	86.6	0.18
Huron	961	1/26/18	7/6/20	66.2	5.9	17.7	9.0	1.2	62.9	0.31
Lost Creek	11	11/12/07	7/4/20	77.5	8.6	7.9	4.3	1.8	63.8	0.69
Maumee	16,388	1/10/75	7/4/20	73.3	6.3	6.5	10.6	3.2	80.6	0.30
Muskingum	19,215	4/11/94	7/4/20	23.6	18.8	43.0	12.4	2.2	17.7	0.32
Portage	1108	8/30/10	7/4/20	84.4	1.3	4.5	9.0	0.8	85.0	0.19
Raisin	2698	3/6/82	3/16/20	49.6	18.7	11.0	10.8	10.0	61.3	0.42
Rock Creek	90	1/18/83	7/4/20	71.9	7.8	11.4	8.8	0.2	77.2	0.41
Sandusky	3239	12/7/74	9/30/04	77.6	4.3	8.8	8.1	1.2	80.3	0.37
Scioto	9965	4/23/96	7/4/20	61.7	8.6	10.9	17.3	1.5	63.4	0.35
Tiffin	1061	4/23/08	7/4/20	60.5	14.8	8.9	7.5	8.3	59.7	0.36
Turkey	300	4/30/18	7/6/20	89.5	1.0	3.0	6.3	0.2	98.7	0.43
Vermilion	679	11/12/00	7/21/08	72.8	-[c]	25.4	1.0	0.8	67.3	0.27
West	40	4/30/18	7/1/20	92.3	0.6	2.0	5.0	0.1	99.3	0.39
Wolf	64	9/24/18	7/6/20	12.0	7.5	28.8	48.1	3.6	65.6	0.20

[a] PDSC refers to poor drainage soil class (i.e., poorly drained, somewhat poorly drained, and very poorly drained) found in the USDA Soil Survey Geographic Data Set.

[b] DD refers to drainage density calculated using the USGS National Hydrography Data Set; (c) pasture is not separated from agriculture.

Table 3
The Akaike information criterion values for regression model selection.

Watershed	Model number[a]								
	1	2	3	4	5	6	7	8	9
Beaver Creek	4.103	4.104	4.086	2.973	4.089	2.972	2.973	2.973	2.971*[b]
Blanchard	1.328	1.323	1.321	1.303	1.317	1.293	1.297	1.288	1.287*
Chickasaw	3.752	3.707	3.749	3.445	3.703	3.41	3.437	3.401	3.399*
Coldwater	3.533	3.528	3.534	3.124	3.529	3.114	3.124	3.114	3.109*
Cuyahoga	0.517	0.512	0.517	0.458	0.512	0.455	0.458	0.455	0.453*
Grand	2.429	2.421	2.419	2.325	2.41	2.316	2.314	2.304	2.299*
Great Miami	0.883	0.871	0.801	0.793	0.785	0.792	0.701	0.697	0.689*
Honey Creek	2.080	2.070	2.047	2.043	2.035	2.038	2.012	2.007	1.931*
Huron	1.669	1.519	1.662	1.633	1.505	1.505	1.627	1.493*	1.494
Lost Creek	2.657	2.520	2.615	2.623	2.491	2.497	2.568	2.458*	2.459
Maumee	3.199	3.01	3.181	3.069	2.981	2.901	3.055	2.878	2.877*
Muskingum	1.721	1.693	1.706	1.538	1.679	1.512	1.519	1.492	1.489*
Portage	1.983	1.836	1.980	1.879	1.836	1.772	1.874	1.770	1.753*
Raisin	2.079	1.870	2.061	2.038	1.856	1.858	2.024	1.845	1.837*
Rock Creek	3.241	3.159	3.232	3.063	3.150	3.023	3.051	3.012	3.009*
Sandusky	3.150	2.834	3.137	3.037	2.819	2.783	3.017	2.763	2.759*
Scioto	0.960	0.937	0.799	0.878	0.759	0.872	0.714	0.698	0.698*
Tiffin	2.307	2.089	2.301	2.276	2.082	2.077	2.264	2.066	2.025*
Turkey	2.387	2.078	2.386	2.361	2.081	2.065*	2.354	2.068	2.066
Vermilion	3.222	3.214	3.153	3.181	3.134	3.169	3.121	3.100	3.100*
West	2.496	2.332	2.425	2.486	2.254	2.327	2.396	2.233	2.226*
Wolf	2.09	2.038	2.094	1.581	2.042	1.58	1.583	1.582	1.568*

[a] Models 1–9 were defined in Table 2.
[b] * indicates that the corresponding model was selected based on AIC.

the scatter plot are evenly distributed around the 1:1 line. In contrast, in the Maumee watershed (the "unsatisfactory" case, Fig. 5(b)), many points lie above the 1:1 line, indicating overestimations. This overestimation might be related to the inadequate fit between log concentration and log discharge, as defined in Table 1. This finding supports Hirsch [15], who demonstrated that an inaccurate quadratic relationship between log concentration and log discharge can result in significant underestimation or overestimation at high discharges, depending on the direction of the curvature.

3.2. Residual analysis

For a regression model to be considered reliable, it is essential to ensure that the assumptions of residual normality, independence, and homoscedasticity are satisfied [25]. In the applications of the regression relationship between flow and nitrate + nitrite concentrations, the assumptions of (model) residual normality and independence were satisfied at all monitoring stations. The assumptions of residual homoscedasticity were met for the 14 watersheds labeled as "satisfactory." However, in the eight watersheds labeled as "unsatisfactory," model residuals were found to be heteroscedastic, rather than homoscedastic or having constant variance (fig. 6 and S1). For instance, in the Blanchard watershed, when segmented into two groups based on an estimated ln(Load) value of 8, the variances of the residuals for both groups were similar, at 0.21 and 0.22 (Fig. 6(a)). Conversely, in the Rock Creek watershed, the group with estimated ln(Load) values less than 3 had a residual variance of 1.70, while the group with values of 3 or higher had a variance of 0.90 (Fig. 6(b)). This indicates that the residual variance is not consistent. In the cases of Maumee, Rock Creek, and Sandusky, the observed concentrations (or the residuals) were found to be systematically associated with the LOADEST estimates (fig. 6(b) and S1 (b)).

In addition, the variations of the nitrate + nitrite concentrations, especially for very low flow, were much higher at the "unsatisfactory" stations (Fig. 7(b)) compared to those of the "satisfactory" ones (Fig. 7(a)). For example, in the Maumee watershed, the standard deviation of log-transformed nitrate + nitrite concentrations was 0.22 when total runoff depths were greater than 100 m^3/s, and the standard deviation changed substantially to 0.74 when the runoff depth was less than the threshold. The findings suggested that the linear or quadratic form (Table 1) might be unable to represent the relationship between flow and nitrate + nitrite concentrations due to the high variation of these concentrations and complicated hydrological and hydraulic processes associated with the nitrate + nitrite transport (Fig. 7). This finding is supported by Lee et al. [20] and Hirsch [15], who revealed that regression methods could overestimate nitrate + nitrite loads because of the high variability of concentrations.

3.3. Relationship between model accuracy and watershed characteristics

The high concentration variances of the low flow might be associated with the landscape characteristics of the study watersheds. To identify the characteristics of watersheds to which the regression models may not be applicable, we compared the hydrological features of the "satisfactory" and "unsatisfactory" groups, including drainage area and density, land use, the sizes of areas with poor drainage class, and soil textures. The *t*-test was conducted to test the significance of the difference between the means of the two groups

Table 4
The best predictive models identified by the LOADEST for estimating nitrate + nitrite loads from streamflow discharge and time.

Watershed	Model number	Equation	R^2
Beaver Creek	9	$\ln(Load) = 1.6046 + 1.2370\ \ln\widehat{Q} + 0.0139\ln\widehat{Q}^2 - 2.0658\ \sin(2\pi dtime) + 1.2534\ \cos(2\pi dtime) - 0.0501 dtime - 0.1111 dtime^2$	0.90
Blanchard	9	$\ln(Load) = 7.7208 + 0.8433\ \ln\widehat{Q} + 0.0225\ln\widehat{Q}^2 + 0.1009\ \sin(2\pi dtime) + 0.0773\ \cos(2\pi dtime) - 0.0091 dtime + 0.0013 dtime^2$	0.87
Chickasaw	9	$\ln(Load) = 3.0196 + 1.2745\ \ln\widehat{Q} - 0.0378\ln\widehat{Q}^2 - 0.4229\ \sin(2\pi dtime) - 1.2197\ \cos(2\pi dtime) + 0.0380 dtime - 0.0067 dtime^2$	0.87
Coldwater	9	$\ln(Load) = 3.0223 + 1.2564\ \ln\widehat{Q} - 0.0318\ln\widehat{Q}^2 - 1.0830\ \sin(2\pi dtime) - 0.7209\ \cos(2\pi dtime) + 0.0068 dtime + 0.0210 dtime^2$	0.83
Cuyahoga	9	$\ln(Load) = 8.2512 + 0.4697\ \ln\widehat{Q} + 0.0212\ln\widehat{Q}^2 + 0.0556\ \sin(2\pi dtime) + 0.0903\ \cos(2\pi dtime) - 0.0006 dtime + 0.0001 dtime^2$	0.62
Grand	9	$\ln(Load) = 5.3274 + 1.1509\ \ln\widehat{Q} + 0.0254\ln\widehat{Q}^2 + 0.0441\ \sin(2\pi dtime) - 0.3578\ \cos(2\pi dtime) + 0.0155 dtime - 0.0021 dtime^2$	0.88
Great Miami	9	$\ln(Load) = 9.9501 + 1.0678\ \ln\widehat{Q} - 0.0231\ln\widehat{Q}^2 - 0.1679\ \sin(2\pi dtime) + 0.0091\ \cos(2\pi dtime) - 0.0159 dtime + 0.0007 dtime^2$	0.91
Honey Creek	9	$\ln(Load) = 6.1303 + 1.1621\ \ln\widehat{Q} - 0.0189\ln\widehat{Q}^2 - 0.0231\ \sin(2\pi dtime) + 0.1704\ \cos(2\pi dtime) - 0.0095 dtime - 0.0012 dtime^2$	0.91
Huron	8	$\ln(Load) = 7.7146 + 1.3094\ \ln\widehat{Q} - 0.1176\ln\widehat{Q}^2 - 0.0920\ \sin(2\pi dtime) - 0.0245\ \cos(2\pi dtime) + 0.0917 dtime$	0.90
Lost Creek	8	$\ln(Load) = 1.6880 + 1.2220\ \ln\widehat{Q} - 0.0632\ln\widehat{Q}^2 + 0.2238\ \sin(2\pi dtime) + 0.1107\ \cos(2\pi dtime) + 0.0467 dtime$	0.89
Maumee	9	$\ln(Load) = 10.2003 + 1.5070\ \ln\widehat{Q} - 0.2112\ln\widehat{Q}^2 - 0.2697\ \sin(2\pi dtime) - 0.4980\ \cos(2\pi dtime) - 0.0124 dtime - 0.0002 dtime^2$	0.83
Muskingum	9	$\ln(Load) = 9.8073 + 1.2422\ \ln\widehat{Q} - 0.0899\ln\widehat{Q}^2 - 0.3249\ \sin(2\pi dtime) + 0.0900\ \cos(2\pi dtime) - 0.0096 dtime + 0.0006 dtime^2$	0.86
Portage	9	$\ln(Load) = 7.7992 + 1.1984\ \ln\widehat{Q} - 0.0723\ln\widehat{Q}^2 - 0.0329\ \sin(2\pi dtime) - 0.2349\ \cos(2\pi dtime) + 0.0111 dtime - 0.0110 dtime^2$	0.91
Raisin	9	$\ln(Load) = 8.3968 + 1.6804\ \ln\widehat{Q} - 0.2314\ln\widehat{Q}^2 + 0.0683\ \sin(2\pi dtime) + 0.0800\ \cos(2\pi dtime) - 0.0066 dtime - 0.0005 dtime^2$	0.89
Rock Creek	9	$\ln(Load) = 4.3829 + 1.4118\ \ln\widehat{Q} - 0.0908\ln\widehat{Q}^2 - 0.3590\ \sin(2\pi dtime) - 0.5736\ \cos(2\pi dtime) - 0.0108 dtime + 0.0006 dtime^2$	0.79
Sandusky	9	$\ln(Load) = 8.5087 + 1.5832\ \ln\widehat{Q} - 0.2227\ln\widehat{Q}^2 + 0.3535\ \sin(2\pi dtime) - 0.1861\ \cos(2\pi dtime) + 0.0166 dtime + 0.0009 dtime^2$	0.87
Scioto	9	$\ln(Load) = 10.0630 + 1.0146\ \ln\widehat{Q} - 0.0396\ln\widehat{Q}^2 - 0.1482\ \sin(2\pi dtime) + 0.0403\ \cos(2\pi dtime) - 0.0206 dtime + 0.0002 dtime^2$	0.91
Tiffin	9	$\ln(Load) = 7.7600 + 1.5831\ \ln\widehat{Q} - 0.2150\ln\widehat{Q}^2 - 0.1120\ \sin(2\pi dtime) + 0.0649\ \cos(2\pi dtime) + 0.0203 dtime - 0.0136 dtime^2$	0.89
Turkey	6	$\ln(Load) = 5.7967 + 1.4002\ \ln\widehat{Q} - 0.1071\ln\widehat{Q}^2 - 0.1367\ \sin(2\pi dtime) + 0.0656\ \cos(2\pi dtime)$	0.94
Vermilion	9	$\ln(Load) = 5.5350 + 1.4559\ \ln\widehat{Q} - 0.0354\ln\widehat{Q}^2 + 0.3063\ \sin(2\pi dtime) - 0.0129\ \cos(2\pi dtime) - 0.1466 dtime + 0.0079 dtime^2$	0.83
West	9	$\ln(Load) = 2.9573 + 1.4346\ \ln\widehat{Q} - 0.0539\ln\widehat{Q}^2 - 0.1888\ \sin(2\pi dtime) - 0.0340\ \cos(2\pi dtime) - 0.3982 dtime - 0.2143 dtime^2$	0.95
Wolf	9	$\ln(Load) = 4.3081 + 1.3726\ \ln\widehat{Q} - 0.0758\ln\widehat{Q}^2 + 0.0500\ \sin(2\pi dtime) - 0.6197\ \cos(2\pi dtime) + 0.0549 dtime + 0.3452 dtime^2$	0.87

Note: $\ln\widehat{Q} = \ln(\text{streamflow}) - \text{center of }\ln(\text{streamflow})$; *dtime* = decimal time – center of decimal time; the center of data $T = \overline{T} + \frac{\sum (T-\overline{T})^3}{2\sum (T-\overline{T})^2}$, and $\overline{T}$ = the mean of the data T [25].

at a significance level of 5 % (Fig. 8). Only the size of agricultural land use of the unsatisfactory group was significantly greater than that of the satisfactory group ($p < 0.05$) (Fig. 9. Such findings indicate that the high concentration variances of the low flow found in the unsatisfactory group (Fig. 7) might be associated with the agricultural management practices implemented in the watersheds. This finding is supported by Castillo and Brunzell [58], who found that the variability of nitrate concentration was more prominent in agriculture-dominant watersheds than in other watersheds. Nutrient supply (or input) is often highly variable over time in agricultural areas due to seasonal applications of fertilizer, variations in the patterns of nutrient transport through soils and groundwater, and the efficacy of denitrification [16]. For instance, nitrate + nitrite concentrations can increase rapidly during the growing season due to applications of fertilizer, and they can decrease quickly either with denitrification, washout during rain events, and/or dilution effects by rain and irrigation water. In our analysis, however, the *t*-test was conducted based on 22 watersheds, and the majority of the watersheds are covered mainly by agricultural land uses. It is worth noting that the "satisfactory" group also includes watersheds with

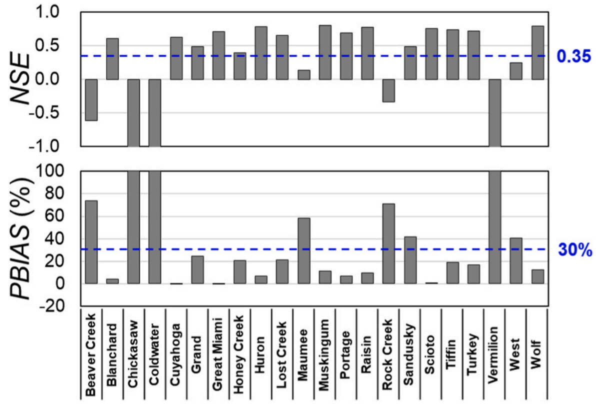

Fig. 3. Comparison of the performance statistics (*NSE* and *PBIAS*) on a daily scale across the 22 study watersheds.

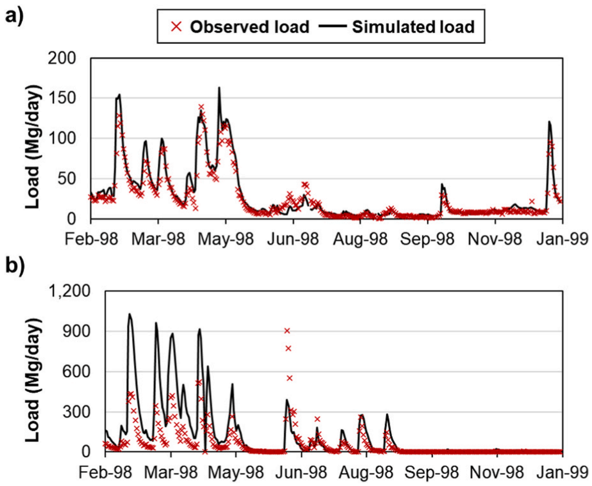

Fig. 4. Daily variations in nitrate + nitrite load estimated from the LOADEST: (a) a "satisfactory" case (the Muskingum watershed) and (b) an "unsatisfactory" case (the Maumee watershed).

substantial agricultural land uses (e.g., Turkey). Therefore, future studies may further investigate additional factors including geomorphological and geophysical features that contribute to high variances in the nutrient concentrations of low flow.

4. Discussion

The accuracy of the regression relationship between flow discharge and constituent loads in streams should be dependent upon various factors, including constituent types, watershed characteristics, and sampling methods and strategies. The results of this study indicated that the use of the regression relationship offered by LOADEST could provide accurate nitrate + nitrite load estimates at only 64 % of the monitoring stations or the watershed outlets. The "unsatisfactory" cases were found at 36 % of the stations where the regression relationship overestimated the upper ranges of the load estimates (Figs. 3–5). Heteroscedastic residuals were commonly found at the stations where poor accuracy was obtained, indicating that severe residual heteroscedasticity might be the key assumption determining the applicability of the regression relationship (fig. 6 and S1). Even when the load or concentration data were log transformed to remedy the heteroscedasticity in the application of the regression relationship (or LOADEST; Table 4), it still remained in the scaled data (Fig. 7). Relationships between model accuracy and watershed characteristics revealed that high variances in concentrations were closely associated with agricultural areas (Fig. 8). This suggests that heteroscedasticity might occur where nutrient input is often highly variable over time.

This study used daily flow and nutrient concentration data obtained from NCWQR to prepare the reference nitrate + nitrite loads (observed loads) to be compared with estimates made using the regression relationship. In practice, however, precise water quality measurements are often not available. Although flow hydrographs are commonly constructed using rating curves and flow depth sensing data, water quality analyses often suffer from the lack of long-term observation records. Additionally, water quality is typically sampled on a weekly or monthly basis in a relatively small number of watersheds as compared to more frequent flow monitoring. To

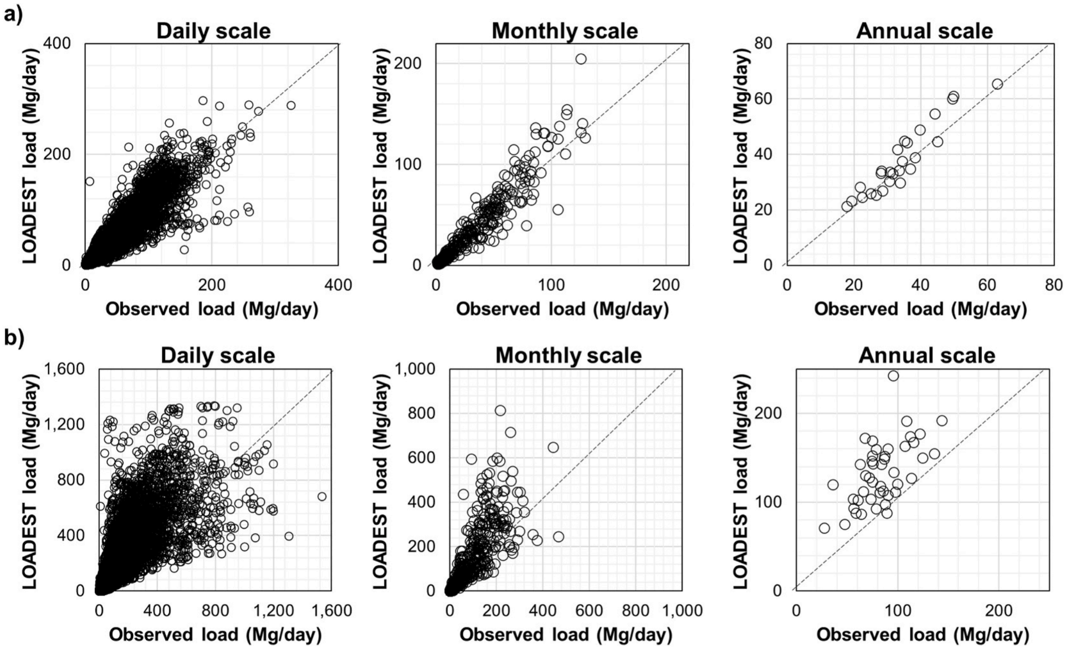

Fig. 5. Comparison between observed and estimated nitrate + nitrite loads: (a) a satisfactory case (the Muskingum watershed) and (b) an unsatisfactory case (the Maumee watershed).

analyze the impacts of these data limitations, we investigated how the length of records (2, 5, 10, 15, 20, 25, and all years) and sampling frequencies (one sample per 1, 3, 7, 14, and 30 days) affect the performance of the regression models (Fig. 10). In the "satisfactory" cases (Muskingum and Raisin in Fig. 10(a)), model performance statistics tend to improve with increases in the length of observations. This result aligns with the findings of Her and Chaubey [13], which demonstrated that extending the calibration period could enhance the accuracy of hydrological predictions when additional information about the hydrology and water quality of a watershed was considered in parameter estimation. Conversely, longer calibration periods did not improve performance in the "unsatisfactory" cases (Maumee and Rock Creek in Fig. 10(a)); in these watersheds, model performance was consistently poor, regardless of the length of the observation period.

When examining results based on changes in sampling frequency (Fig. 10(b)), the "satisfactory" cases consistently demonstrated excellent performance across all sampling intervals. In the Muskingum watershed, for example, despite the large difference in the number of measurements between a 1-day interval (the number of samples: 9144) and a 30-day interval (the number of samples: 305), the *NSEs* were high (0.78 and 0.76, respectively) in both cases. This suggests that it is more important to include information about wet and dry seasons to obtain robust estimates of model parameters rather than simply increasing the number of observations [59–61]. Moreover, the finding implies that statistical methods, including regression models and LOADEST, can be a quick and sound solution for load estimation, especially when mechanistic modeling approaches are not feasible and when both sampling intervals and monitoring periods are long. Conversely, the performance was consistently poor in the "unsatisfactory" watersheds, regardless of the sampling frequencies. These results suggest that the characteristics of the watershed should be carefully considered when establishing the regression relationship between flow discharge and constituent loads.

This study found that the regression relationship provided acceptable accuracy statistics at only 14 of the 22 study watersheds. Many factors may be present that affect the accuracy of regression analysis (or LOADEST), such as the model's intrinsic (or structural) limitations, errors in water quality observations and flow rating curves (particularly associated with high flow), and the seasonality of agricultural management practices including tile drainage and fertilizer application. Previous studies have demonstrated that assumptions of residual homoscedasticity, as well as fixed relationships between water quality concentration and discharge, are the primary reasons for the failure of regression models [15,16]. Although the nitrate + nitrite loads were scaled using a log transformation in the application of the regression models (or LOADEST), the heteroscedasticity was persistent in this study (Fig. 7). In addition, the monitoring data may contain errors and uncertainty, which might contribute to the heteroscedasticity of the residuals [62]. For example, nitrate + nitrite concentrations are not responsive to changes in flow discharge when the flow is low (Fig. 7(b)), which implies that the concentration measurements might include systematic errors. The flow rating curves are known to include systematic or structural errors, and the contributions of nonsystematic errors to uncertainty was found to be negligible [63]. Hirsch [15] attempted to consider the heteroscedasticity by assuming the residuals (or errors) to vary over time, but the issue could not be solved in some of the study watersheds. Furthermore, fertilizer is one of the contributors to the high nutrient concentrations and loads in the study areas [56,64]. The decision of application timings and rates of fertilizers is made considering many factors, and their loading to downstream waterbodies is controlled by soil water content and streamflow routing. Thus, the amount of fertilizer that can be lost or

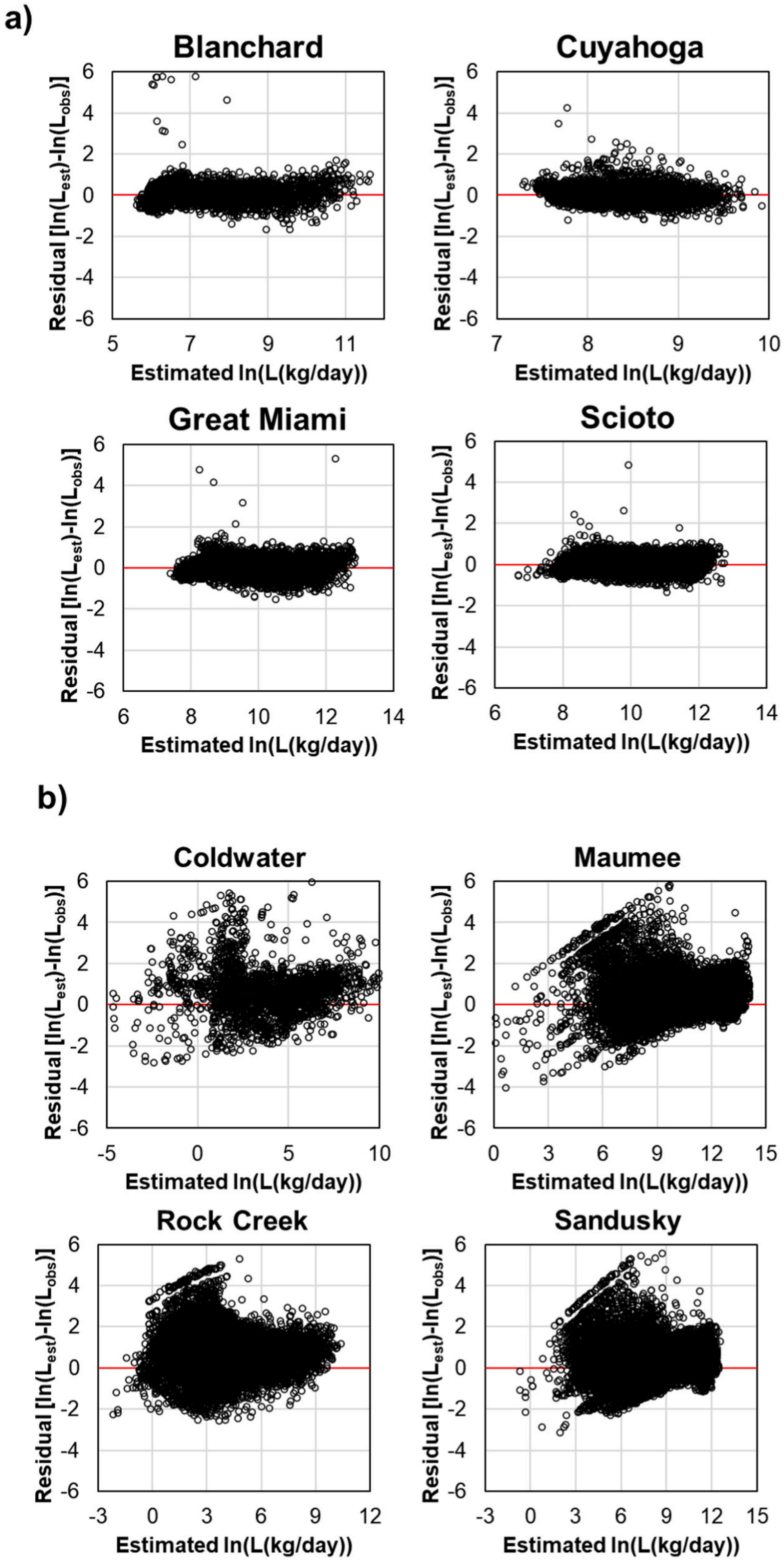

Fig. 6. Relationship between the daily LOADEST estimates and their errors (or residuals); (a) "satisfactory" stations and (b) "unsatisfactory" stations. Relationships concerning the stations not featured in this figure are available in fig. S1 ofthe supplementary material.

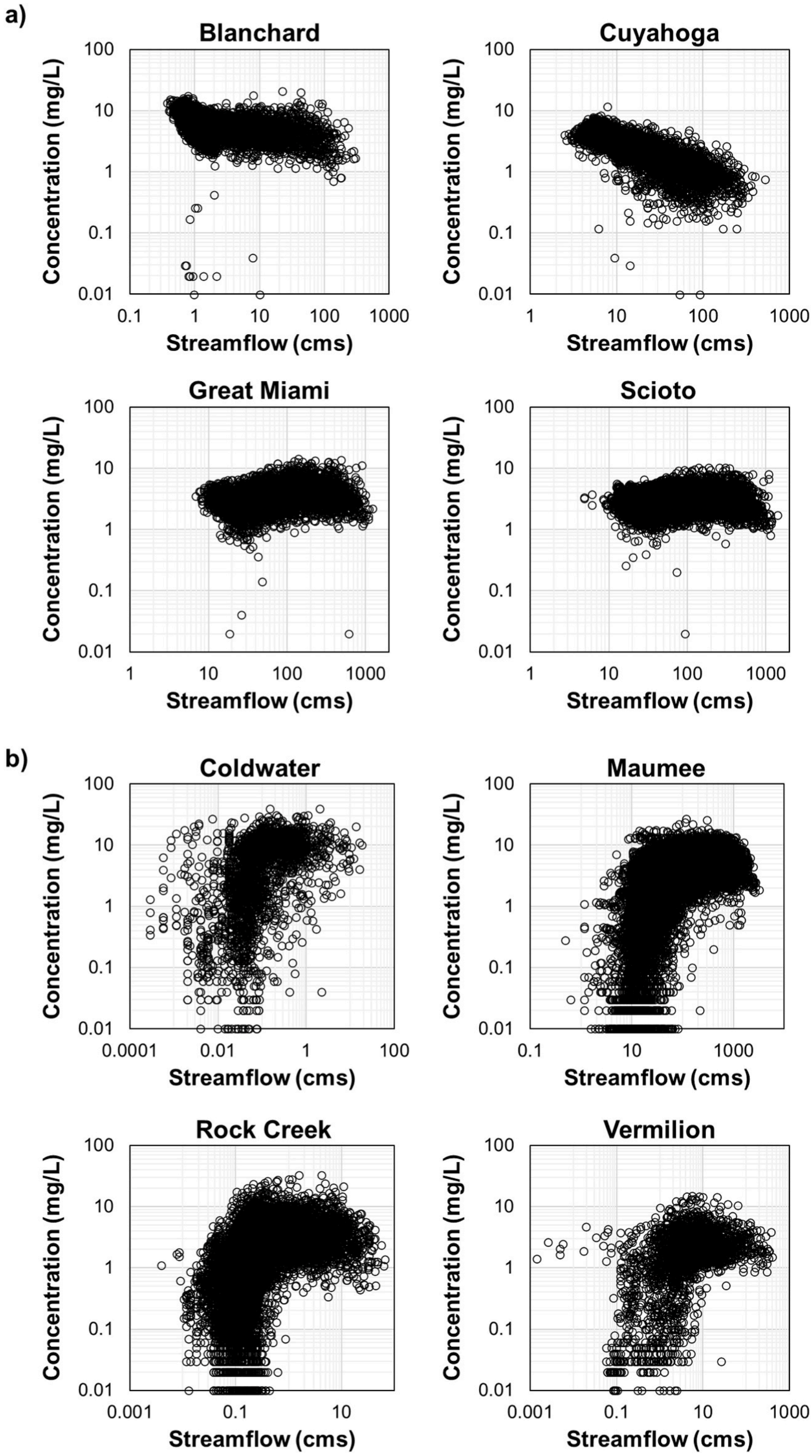

Fig. 7. Relationships between observed nitrate + nitrite concentrations and total runoff discharges at a daily scale; (a) "satisfactory" cases and (b) "unsatisfactory" cases.

washed out by rainfall events is dependent on hydrological processes as well as fertilizer application practices, which adds further variations and heteroscedasticity to the data. For example, a small rainfall event may wash out a relatively large amount of fertilizer applied to fields if it comes directly after the fertilizer application, and the opposite is also the case.

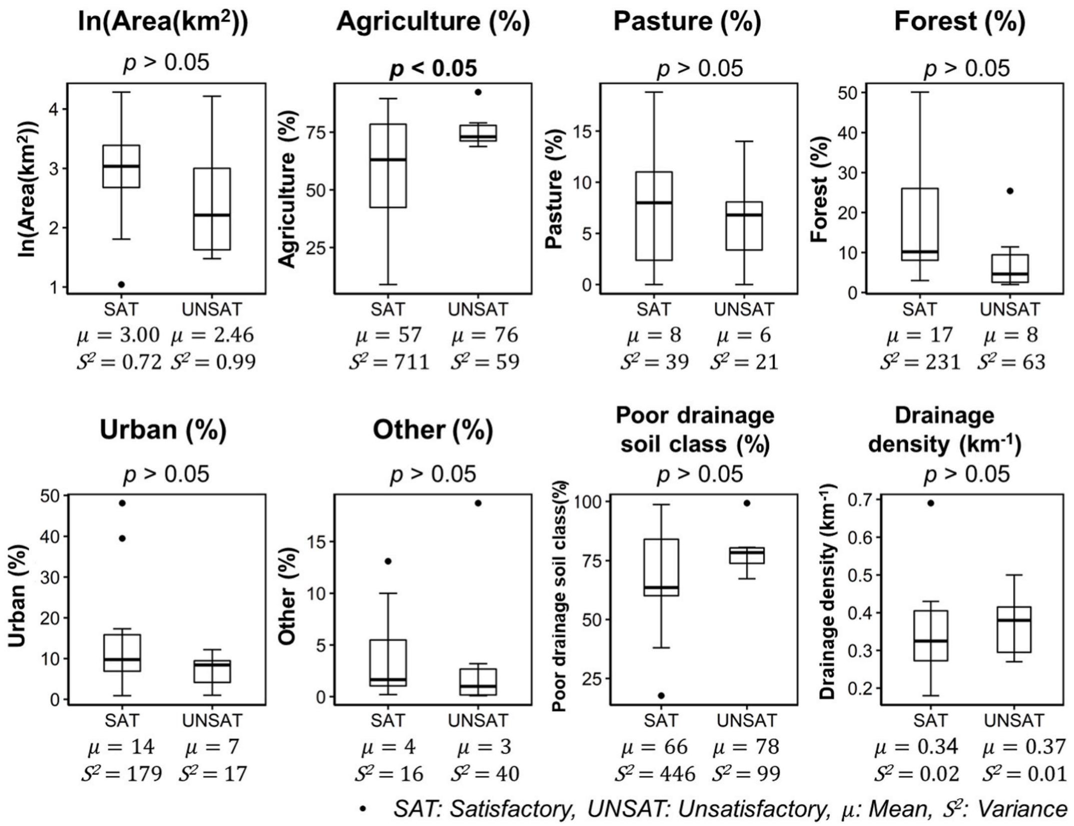

Fig. 8. Comparison between the watershed characteristics of the satisfactory and unsatisfactory groups.

Studies attempted to address the limitations observed in the regression relationship by incorporating additional explanatory variables beyond time and discharge used in LOADEST or by introducing functions beyond the basic linear, quadratic, and logarithmic functions. For instance, Vecchia et al. [65] proposed the "flow anomaly" variables that are computed based on daily discharge records to account for flow-related variability in water quality concentrations. Zhang and Ball [66] developed a set of modified WRTDS models with flow anomaly and reported the accuracy improvement of load estimates. To address nonlinearities in relationships and the skewness of water quality data, Biagi et al. [1] used GAMs, which apply smoothing functions for their covariates without being restricted to a set form. However, it should be noted that the flexibility of such approaches can increase the risk of overfitting, particularly if the model becomes overly tailored to the calibration data. Future studies may investigate how to reduce uncertainty that originated from adopting new variables or smoothing functions.

The application results implied that there might be additional fundamental reasons for why the statistical methods failed accurately to estimate the nitrate + nitrite loads from the relationship between flow and concentrations. The regression equation relates nutrient loads to flow discharges observed on the same day, which is reasonable because the amount of nutrient that can be transported with streamflow is often determined by the flow discharge rates. Such an approach predicts nutrient (or sediment) loads on the basis of the transport capacity (capacity-limited) concept, assuming the amount of nutrient (or sediment) transportable by flowing water is limited by the flow energy rather than by the amount of nutrient loaded from the sources to the flow (supply-limited concept) [67]. The transport capacity concept assumes unlimited supply; thus, flow will be under an equilibrium condition where nutrient loading and discharging rates are equal. In reality, however, the nutrient transport process may not be fully explained by only one of the two assumptions or concepts: capacity- and supply-limited transport regimes [68]. For instance, the regression relationship between flow discharge rates and nutrient loads may not hold when the supply of nutrients is limited in highly urbanized areas during a large storm event. Moreover, nutrient supply may vary over time in agricultural areas due to seasonal fertilizer applications, temporal and spatial variations of soil water content, and resulting variations in surface water and groundwater movements. Furthermore, nitrates and nitrites are soluble, rather than being attached to particles and transported with them; thus, the capacity-limited regime or transport capacity concept that has been commonly used to describe sediment (or bed load) transport may not apply to explaining the transport of nitrate + nitrite loads [68]. Especially when agricultural conservation practices are implemented intensively to reduce the amount of sediment and nutrient to be transported to downstream waterbodies, large flow discharge may not necessarily indicate great nitrate + nitrite loads. Thus, while statistical models offer valuable information when mechanistic models cannot be applied, they must be used judiciously and in conjunction with a understanding of the underlying hydrological processes and management practices that can affect the processes.

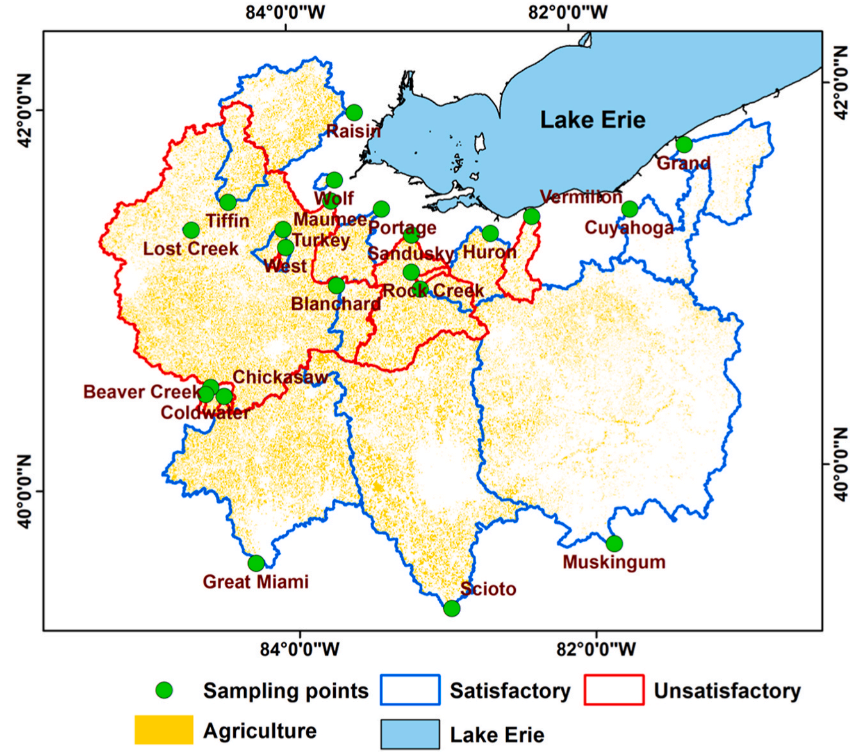

Fig. 9. Locations and agricultural land use size of "satisfactory" and "unsatisfactory" cases.

5. Conclusion

This study investigated the applicability of the regression relationship in estimating nitrate + nitrite loads from flow discharge and nitrate + nitrite concentrations. The results indicated that the regression models offered by LOADEST were applicable at only 64 % of the 22 monitoring stations in the HTLP watersheds. The regression relationship failed to provide acceptable accuracy ($NSE \geq 0.35$ and $|PBIAS| \leq 30.0\%$) of nitrate + nitrite load estimates at the other 36 % of the stations. The unsatisfactory cases were found in watersheds where the variances of nitrate + nitrite concentrations were relatively high at low flow, which contributed to the heteroscedasticity of the residuals and then led to poor accuracy. The results recommend that the assumptions of the regression, especially the residual homoscedasticity assumption, should be carefully investigated when estimating loads from concentrations and flow discharges using the regression relationship. The difference between the watershed features of the satisfactory and unsatisfactory groups was significant only in the sizes of agricultural land uses in which relatively large seasonal variations were found in the nitrate + nitrite concentration measurements. The large seasonal variations might be attributed to nitrogen fertilization. Furthermore, the use of the regression relationships accepts the transport capacity or capacity-limited concept that assumes unlimited nitrate + nitrite loads (or supply), which may not always be the case in reality. Thus, the poor performance of the regression is likely associated with agricultural practices and land uses and the assumption of the nutrient transport mechanism. This implies that additional caution should be taken when applying the regression to areas in which intensive management practices that can affect sediment and nutrient loading and transport processes are implemented.

This study did not merely aim to criticize the limitations of regression models. Instead, we sought to explore the fundamental reasons (i.e., watershed characteristics and the transport capacity concept) that influence the applicability of the regression relationship between flow rates and nitrate + nitrite loads. It is worth noting that the sample size of this study, comprising 22 watersheds, might be considered relatively small. Further research will be necessary to represent a broader range of watersheds or geographic and climate regions.

Data availability statement

The LOADEST model is publicly available, and its installation files can be freely downloaded from this page: https://water.usgs.gov/software/loadest/download/. The water quality data used for this analysis are publicly accessible at: https://ncwqr-data.org/HTLP/Portal. All relevant data used for analysis in this study can be accessed from the following repository: HELIYON-D-23-41979_Dataset. https://osf.io/6r2qx/.

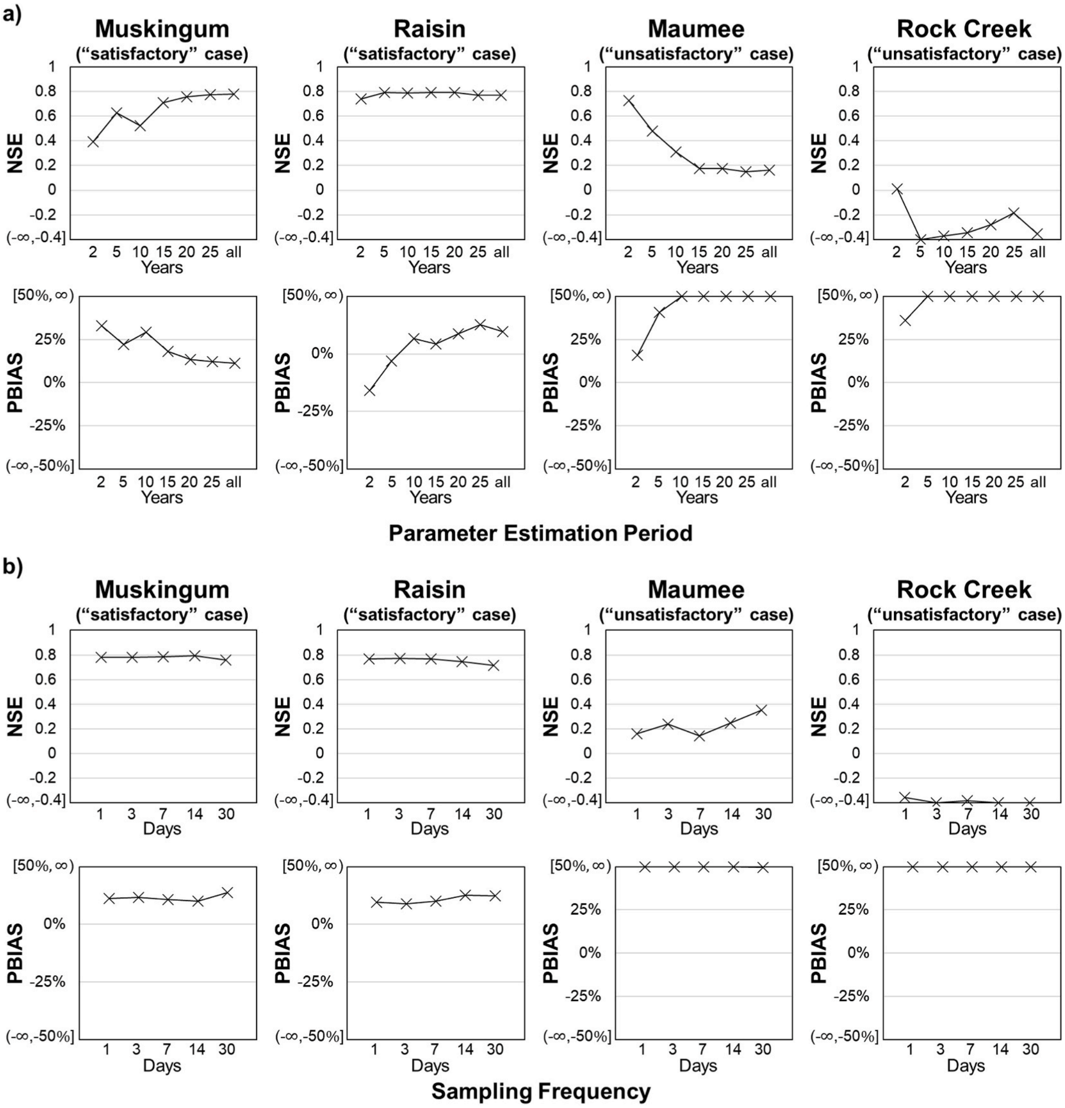

Fig. 10. The model performance statistics at a daily scale with the different sampling periods and frequencies: (a) variations in the length of parameter estimation periods (2, 5, 10, 15, 20, 25, and all years), and (b) variations in sampling frequencies (one sample per 1, 3, 7, 14, and 30 days). Model performance statistics were calculated using all observations (i.e., the entire period).

CRediT authorship contribution statement

Jung-Hun Song: Writing – original draft, Visualization, Validation, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Younggu Her:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Youn Shik Park:** Writing – review & editing, Visualization, Software, Methodology, Formal analysis, Data curation. **Kwangsik Yoon:** Writing – review & editing, Conceptualization. **Hakkwan Kim:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jung-Hun Song reports financial support was provided by National Research Foundation of Korea. Younggu Her reports financial support was provided by National Institute of Food and Agriculture. The authors appreciate Dr. Jane Frankenber's constructive and valuable comments and suggestions that improved this manuscript and study.

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