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Technical Note

Use of Pollutant Load Regression Models with Various Sampling Frequencies for Annual Load Estimation

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Abstract: Water quality data are collected by various sampling frequencies, and the data may not be collected at a high frequency nor over the range of streamflow conditions. Therefore, regression models are used to estimate pollutant data for days on which water quality data were not measured. Pollutant load regression models were evaluated with six sampling frequencies for daily nitrogen, phosphorus, and sediment data. Annual pollutant load estimates exhibited various behaviors by sampling frequency and also by the regression model used. Several distinct sampling frequency features were observed in the study. The first was that more frequent sampling did not necessarily lead to more accurate and precise annual pollutant load estimates. The second was that use of water quality data collected from storm events improved both accuracy and precision in annual pollutant load estimates for all water quality parameters. The third was that the pollutant regression model automatically selected by LOADEST did not necessarily lead to more accurate and precise annual pollutant load estimates. The fourth was that pollutant regression models displayed different behaviors for different water quality parameters in annual pollutant load estimation.

Keywords: annual load estimation; LOADEST; regression model; sampling frequency; water quality data

1. Introduction

Typically, water quality samples are costly to collect and to analyze. Water quality samples are collected by various sampling frequencies [1] and thus may not be collected over the period of streamflow data and further are not typically collected at the same data frequency (or interval) as streamflow data. Few water quality datasets have been collected by frequent water quality sampling (*i.e.*, short sampling intervals) such as on an hourly basis [2]; however, water quality data have often been collected infrequently compared to streamflow data frequencies [3,4].

Thus, water quality data are often estimated using statistical methods such as regression models from measurements made intermittently in a certain period of time [5]. Regression models are used extensively to interpolate intermittent water quality data and are often simple linear forms using logarithmic transformations [6,7]. Various water quality data sampling frequencies have been used to estimate pollutant loads with regression models and to explore what sampling frequencies are appropriate for regression model uses [5,8–11]. Acceptable load estimates were provided by regression models with water quality data collected biweekly or monthly supplemented with storm samples [5,8,9], while in other cases, regression models often provided poor load estimates (*i.e.*, load estimates with large error) when the number of water quality data were small [8] or when water quality datasets did not follow a normal distribution [10]. Moreover, regression models displayed differences of up to 65% in annual nitrate-N load estimates [11].

In addition to sampling frequencies and regression models, water quality parameters are also influential to load estimation, since each water quality parameter has different behaviors in watersheds. Streamflow and total nitrogen concentration displayed poor relationships, and sediment concentration and streamflow showed significant correlation in pasture watersheds [12]. In another study, baseflow was a major source of nitrate loads to streamflow since nitrate concentration and baseflow displayed a proportional relationship; however, orthophosphate concentration was not related to baseflow behavior [13].

LOAD ESTimator (LOADEST) [14] is used to estimate pollutant loads using streamflow data, water quality concentration data, and regression model coefficients using one of 11 regression models. LOADEST has been used to estimate daily pollutant loads for various water quality parameters with various sample sizes (or sampling frequencies) including weekly [15], monthly [16], or bimonthly [17,18] collected water quality samples. The Load Interpolation Tool (LOADIN) [19] is a web-based tool to estimate pollutant loads from streamflow and intermittent water quality data. LOADIN has the same purpose as LOADEST and requires streamflow and water quality data to estimate pollutant loads. However, LOADIN uses a different regression model and different approach to calibrate the model coefficients.

In this study, the predictive ability of LOADEST and LOADIN was evaluated with six sampling frequencies for three water quality parameters, and appropriate regression models and water quality sampling frequencies were suggested to obtain accurate annual pollutant load estimates.

2. Materials and Methods

2.1. Water Quality Data Collection and Subsampling

Daily streamflow and water quality data were required to compute an observed “true load” and to create subsampled water quality datasets for LOADEST and LOADIN runs. Therefore, daily streamflow and water quality data for nitrogen, phosphorus, and sediment were collected from the National Center for Water Quality Research of Heidelberg University [20] and the USGS Water-Quality Data for the Nation [21] (Figure 1). Daily nitrogen (Total Nitrogen; USGS Water Quality Parameter Code: 91058) data were collected from 21 stations, daily phosphorus (Phosphorus; USGS Water Quality Parameter Code: 91050) data were collected from 69 stations, and daily sediment (Suspended Sediment Discharge; USGS Water Quality Parameter Code: 80155) data were collected from 211 stations (Table 1). The water quality data collected in the study displayed different relationships with streamflow. Correlation coefficients (Equation (1)) were computed to provide the relationships between streamflow and concentration data (Figure 2). The averages of correlation coefficients were 0.6 for sediment concentration data, 0.3 for phosphorus concentration data, and 0.2 for nitrogen concentration data. Thus, sediment concentration data were most-closely correlated to streamflow, compared to phosphorus and nitrogen concentration data.

$$\text{Correlation Coefficient} = \frac{\sum(C_i - \bar{C})(F_i - \bar{F})}{\sqrt{(C_i - \bar{C})^2} \sqrt{(F_i - \bar{F})^2}} \tag{1}$$

where C_i is concentration at time step i ; \bar{C} is mean of concentration data; F_i is streamflow at time step i ; and \bar{F} is mean of streamflow data.

Figure 1. Locations of Daily Water Quality Data Stations.

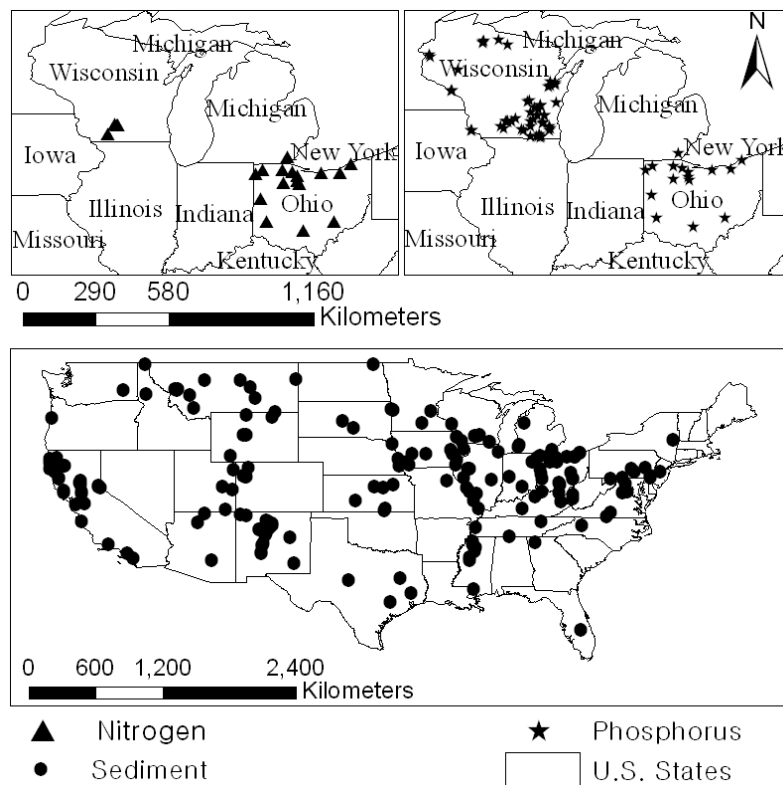
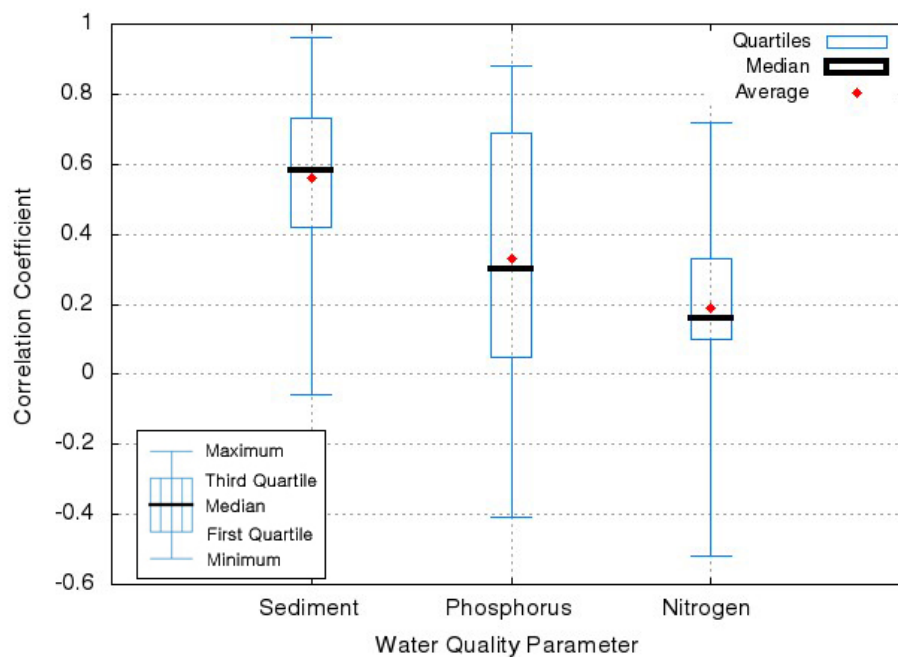


Table 1. Number of stations and daily water quality data values.

Water Quality Parameters	1~10 years	11~20 years	21~37 years	Total
Nitrogen	11 ^a	5 ^a	5 ^a	21 ^a
	10,220 ^b	28,835 ^b	58,035 ^b	97,090 ^b
Phosphorus	59 ^a	5 ^a	5 ^a	69 ^a
	56,940 ^b	28,835 ^b	58,035 ^b	143,810 ^b
Sediment	201 ^a	5 ^a	5 ^a	211 ^a
	423,035 ^b	28,835 ^b	58,035 ^b	509,905 ^b

Notes: ^a number of stations; ^b number of water quality data values.

Figure 2. Correlation Coefficients for Concentrations of Water Quality Parameters with Streamflow (adapted from Park, 2014 [22]).



Six sampling frequencies were established with combinations of fixed intervals and inclusion of storm samples. The first three sampling frequencies represented collecting one water quality sample every week (weekly fixed interval sampling frequency), every two weeks (biweekly fixed interval sampling frequency), and every month (monthly fixed interval sampling frequency).

For fixed interval sampling, water quality data were selected on the same day every week, two weeks, and month so that weekly, biweekly, and monthly sampling had seven, fourteen, and twenty eight variants, respectively. For instance, the first subsampled water quality datasets for the weekly interval frequency were comprised of the water quality data observed on every Monday, while the second subsampled water quality datasets for the weekly interval frequency were comprised of the water quality data observed on every Tuesday. Therefore, seven subsampled water quality datasets were prepared for the weekly interval frequency. The first subsampled water quality datasets for the biweekly interval frequency were comprised of the water quality data observed on every alternate Monday, and the second subsampled water quality datasets for the biweekly interval frequency were comprised of water quality data observed on every alternate Tuesday. Therefore, fourteen subsampled

water quality datasets were prepared for the biweekly interval frequency. The subsampling method for monthly interval frequencies was based on date. For instance, the first subsampled water quality dataset for monthly interval frequencies was comprised of the water quality data observed on the 1st day of each month, and the second subsampled water quality dataset for monthly interval frequencies was comprised of the water quality data observed on the 2nd day of each month.

The other three sampling frequencies termed “mixed interval sampling” included additional samples from within storm events while maintaining the same sampling intervals as the first three frequencies. Storm samples in the study were defined as water quality data collected from peak flows in the “high flow” regime that represent the upper 10 percent of flows for a given analysis period [23].

2.2. Regression Models

The regression model coefficients in LOADEST are calibrated by three statistical methods which are Adjusted Maximum Likelihood Estimation (AMLE), Maximum Likelihood Estimation (MLE), and Least Absolute Deviation (LAD) [14]. The AMLE and MLE methods assume that the calibration model error (or residuals) follows a normal distribution, and allow use of water quality datasets containing censored data [24]. The LAD method is based on the assumption that the errors are independently and identically distributed random variables [25].

LOADEST has 11 regression models, and one of them is selected manually or automatically (model number option 0). The first nine regression models numbered from 1 to 9 (Equations (2)–(10), left-hand side is logarithm pollutant load) are selectable by the automatic regression model selection, but the other regression models numbered 10 and 11 (Equations (11) and (12)) are used to estimate pollutant loads for specific periods defined by users. Therefore, LOADEST was executed ten times for each subsampled water quality dataset with model number 0 to investigate performance for automatic model selection of LOADEST and with model numbers 1 to 9 to evaluate each regression model for manual model selection. Subsampled water quality datasets were used for LOADEST and LOADIN runs.

$$a_0 + a_1 \ln Q \quad (2)$$

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 \quad (3)$$

$$a_0 + a_1 \ln Q + a_2 dtime \quad (4)$$

$$a_0 + a_1 \ln Q + a_2 \sin(2\pi dtime) + a_3 \cos(2\pi dtime) \quad (5)$$

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 dtime \quad (6)$$

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) \quad (7)$$

$$a_0 + a_1 \ln Q + a_2 \sin(2\pi dtime) + a_3 \cos(2\pi dtime) + a_4 dtime \quad (8)$$

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5 dtime \quad (9)$$

$$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5 dtime + a_6 dtime^2 \quad (10)$$

$$a_0 + a_1 per + a_2 \ln Q + a_3 \ln Q per \quad (11)$$

$$a_0 + a_1 per + a_2 \ln Q + a_3 \ln Q per + a_4 \ln Q^2 + a_5 \ln Q^2 per \quad (12)$$

where, a_{0-6} are coefficients; Q is streamflow; $dtime$ is decimal time; and per is the period defined by the user [14].

LOADIN employs a regression model comprised of streamflow, decimal time, and eight model coefficients (Equation (13)). LOADIN finds values of the eight model coefficients that minimize differences between modeled and observed loads using a genetic algorithm and given water quality datasets.

$$L_i = a_1 \cdot Q_i^{a_2} + [1 + \sin(a_3 \cdot dtime_i + a_4)] \cdot a_5 \cdot Q_i + [1 + \cos(a_6 \cdot dtime_i + a_7)] \cdot a_8 \cdot Q_i \quad (13)$$

where, L_i is pollutant load at time step i ; Q_i is streamflow at time step i .

The regression models in LOADEST assume that instantaneous load is an exponential function of data variables (e.g., streamflow) [14]; however, the regression model in LOADIN assumes that instantaneous load is comprised of the pollutant load by flow and the pollutant load varying by time.

Annual pollutant loads estimated by the regression models in LOADEST and LOADIN were compared to annual loads calculated by multiplying daily streamflow by concentration measurements (Equation (14)).

$$\text{Observed Average Annual Load} = \frac{\sum_{i=1}^n Q_i \cdot C_i}{\text{Num.}_{yr}} \quad (14)$$

where, i is day; Q_i is streamflow on day i ; C_i is concentration on day i ; and $Num._{yr}$ is the number of years.

A ratio was used to compare the estimated annual pollutant loads to the observed annual pollutant loads (Equation (15)). A ratio greater than 1.0 indicates that a regression model overestimated annual pollutant load, a ratio smaller than 1.0 indicates that a regression model underestimated annual pollutant load, and a ratio of 1.0 indicates estimated annual pollutant load is the same as observed annual pollutant load.

$$\text{Ratio} = \frac{\text{Estimated Annual Pollutant Load}}{\text{Observed Annual Pollutant Load}} \quad (15)$$

Both accuracy and precision are critical in evaluation of regression models and sampling frequencies, because accuracy indicates the degree of systematic error and precision indicates the degree of dispersion [26,27]. Accuracy and precision were evaluated by comparing means of the ratio of estimate and observed annual pollutant loads and 95% confidence intervals, respectively.

3. Results and Discussion

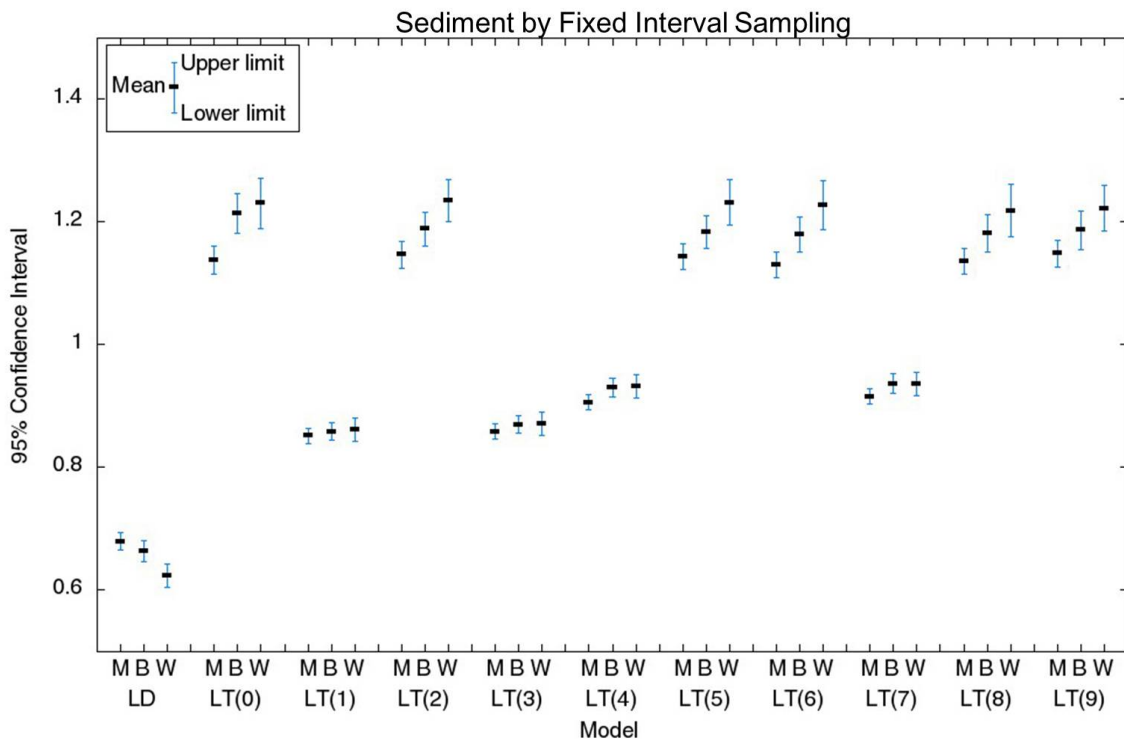
Figure 3 shows variations of 95% confidence intervals of the ratios (Equation (15)) by different sampling frequencies and regression models of LOADIN (LD) and LOADEST (LT). The numbers with LT indicate the LOADEST model number; for instance, LT(3) indicates LOADEST model number 3. Each model in each graph has three 95% confidence intervals; the first 95% confidence interval is for the monthly (M) sampling frequency, the second 95% confidence interval is for the biweekly sampling frequency (B), and the third 95% confidence interval is for the weekly sampling frequency (W).

LOADIN and the regression models numbered 1, 3, 4, and 7 in LOADEST (LT(1), LT(3), LT(4), and LT(7) in Figure 3a,b) were more precise for annual sediment load estimates than the regression models numbered 2, 5, 6, 8, and 9 in LOADEST (LT(2), LT(5), LT(6), LT(8), and LT(9) in Figure 3a,b). However, mean of ratio were not much different with sampling frequencies within each

regression model, which means the accuracy of regression models were similar for annual sediment load estimates (Figure 3a,b).

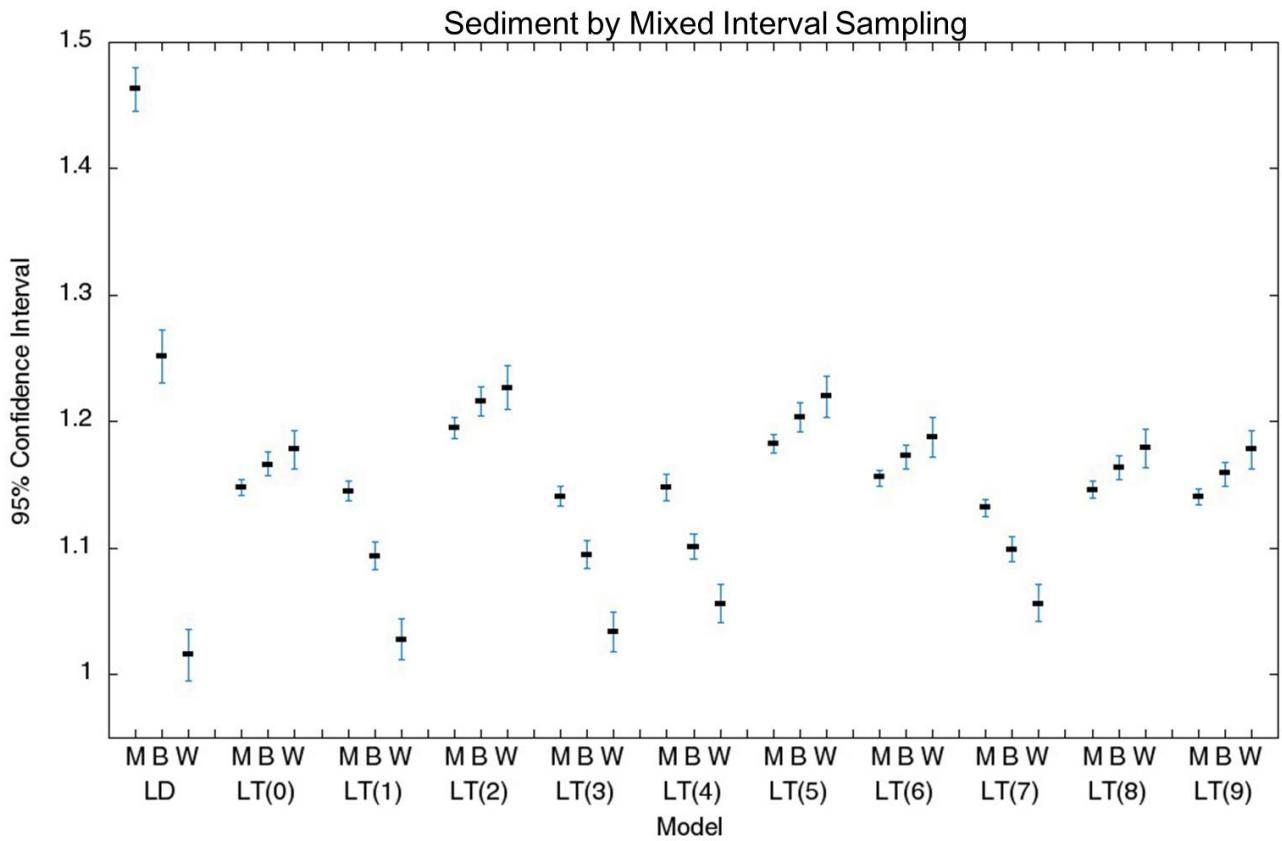
A distinct feature was found in annual sediment load estimation. More frequent sampling led to accurate and less precise annual sediment load estimates with LOADEST models numbered 1, 3, 4, and 7, when comparing the weekly sampling frequency to the monthly sampling frequency (Figure 3a,b). Nevertheless, weekly sampling data typically provided less precise (*i.e.*, wider 95% confidence intervals) annual sediment load estimates than monthly sampling data. Weekly sampling data with LOADEST models numbered 1, 3, 4, and 7 provided smaller differences relative to observed loads compared to monthly sampling data (Figure 3a,b). In other words, use of frequent water quality data with LOADEST models numbered 1, 3, 4, and 7 led to the annual sediment load estimates with smaller differences compared to observed sediment load. However, use of more frequent sampling led to less accurate and less precise annual sediment load estimates with LOADEST models numbered 2, 5, 6, 8, and 9. For instance, weekly sampling frequencies with LOADEST models numbered 2, 5, 6, 8, and 9 displayed wider 95% confidence intervals than monthly sampling frequencies. Thus, it was concluded that more frequent sampling do not necessarily lead to more accurate and precise annual sediment load estimates than use of less frequent sampling.

Figure 3. 95% Confidence Intervals of Estimated to Observed Pollutant Load Ratios. (M: Monthly sampling, B: Biweekly sampling, W: Weekly sampling); (a) Sediment by Fixed Interval Sampling; (b) Sediment by Mixed Interval Sampling; (c) Phosphorus by Mixed Interval Sampling; (d) Phosphorus by Mixed Interval Sampling; (e) Nitrogen by Fixed Interval Sampling; (f) Nitrogen by Mixed Interval Sampling.

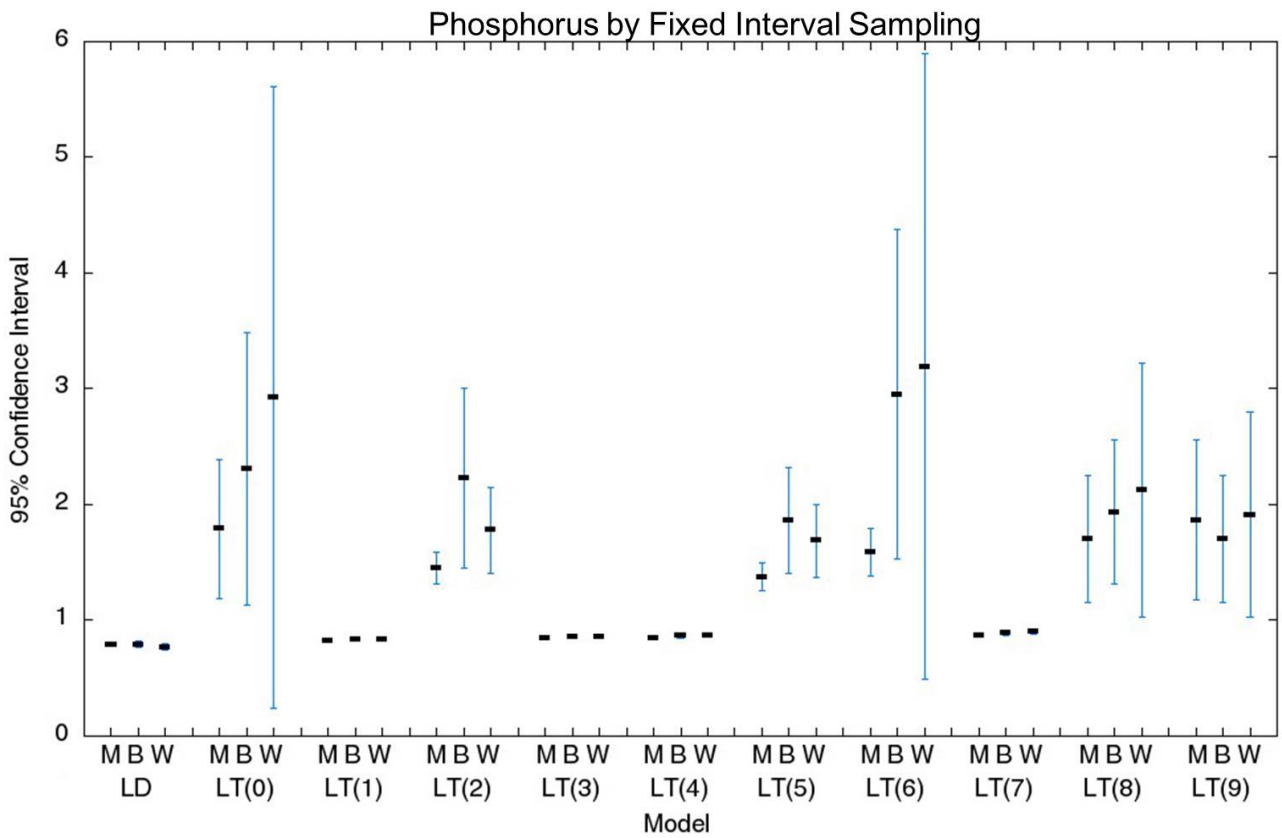


(a)

Figure 3. Cont.



(b)



(c)

Figure 3. Cont.

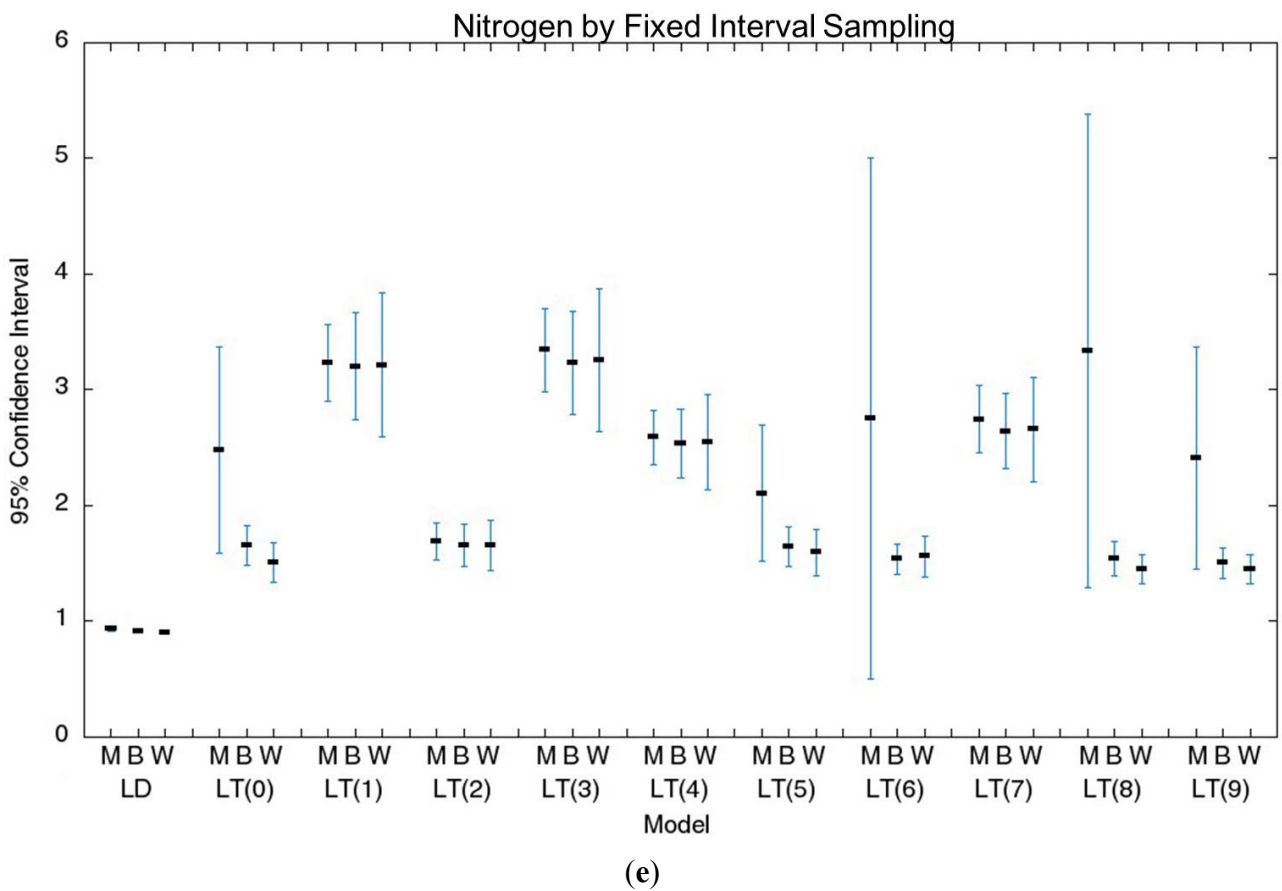
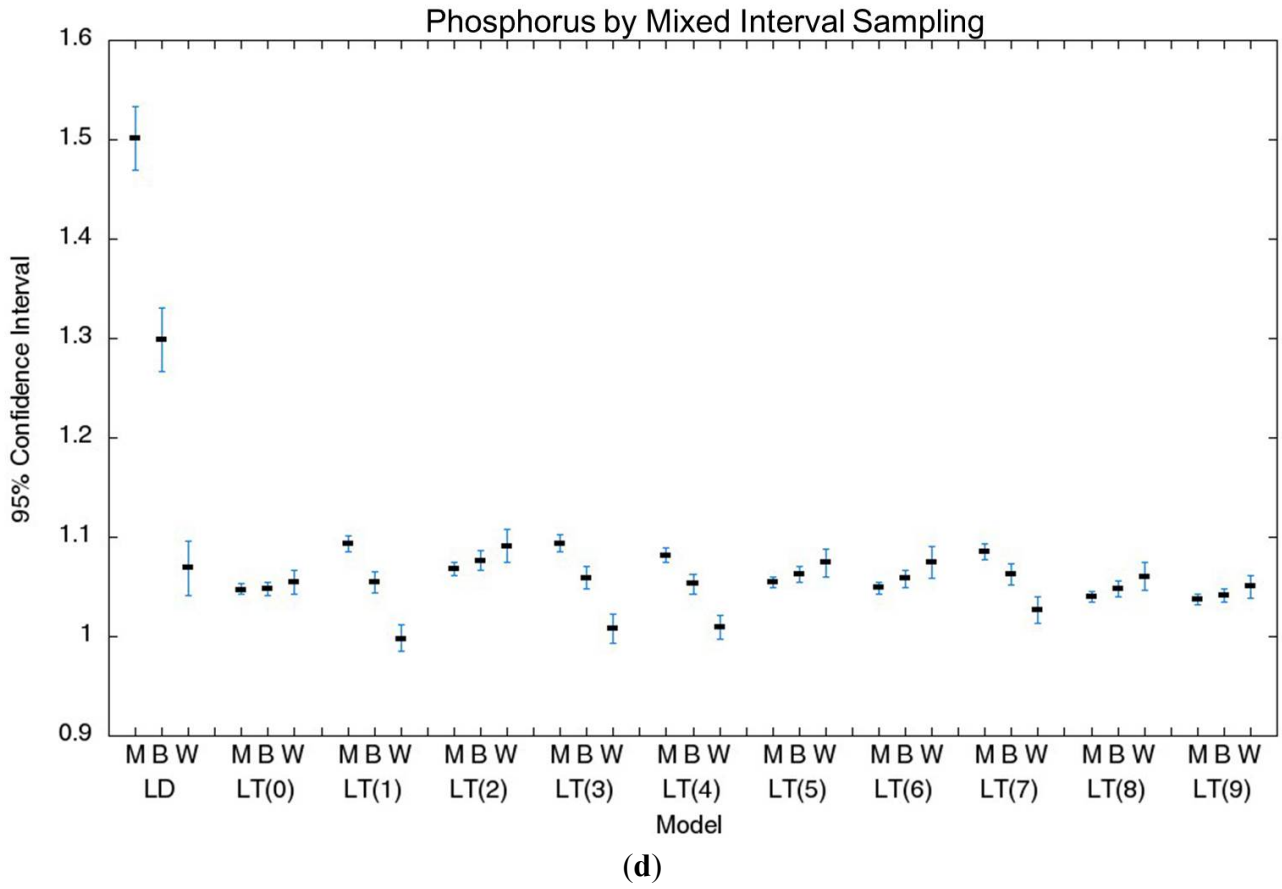
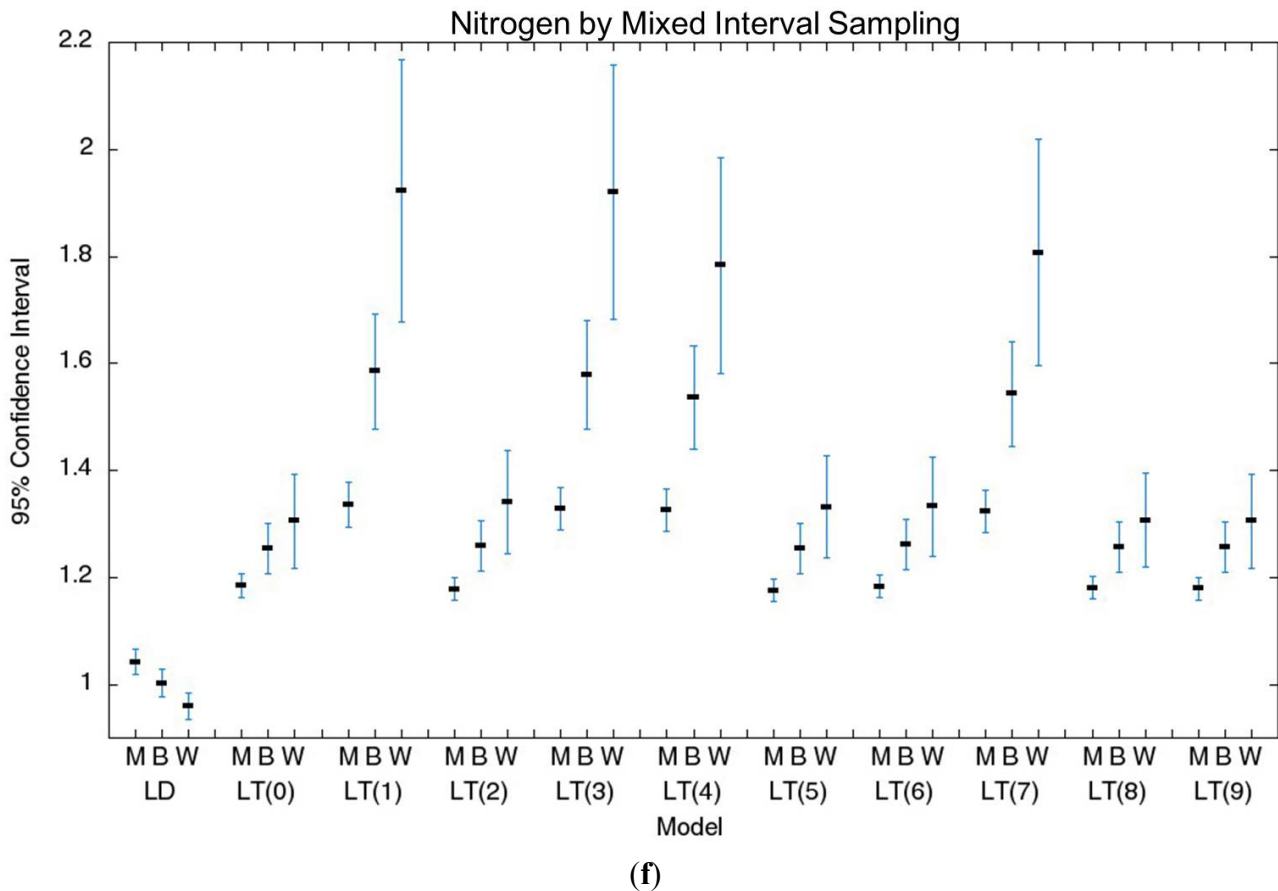


Figure 3. Cont.



LOADIN and regression models numbered 1, 3, 4, and 7 in LOADEST provided more accurate and more precise annual phosphorus load estimates than models numbered 2, 5, 6, 8, and 9 in LOADEST with fixed interval sampling frequencies (Figure 3c and Table 2). Accuracy and precision were improved by including storm samples (Figure 3c,d), this feature corresponds to the other researchers' results [9,11] indicating that storm samples are important in pollutant load estimations.

In nitrogen load estimation, LOADEST provided poorer load estimates than LOADIN, and especially regression models numbered 6, 8, and 9 in LOADEST with monthly fixed sampling frequencies which were less precise than other regression models. Compared to the annual nitrogen load estimates made by LOADEST, LOADIN provided more accurate and more precise load estimates with both fixed interval sampling frequencies and mixed interval frequencies. The biweekly mixed interval sampling frequency for LOADIN displayed the most accurate and precise annual nitrogen load estimates.

The annual pollutant load estimates made by the automatic model selection of LOADEST did not provide the best precision nor accuracy for pollutant load estimation. Annual sediment and phosphorus load estimates made by regression models numbered 1, 3, 4, and 7 in LOADEST were more accurate and precise than those of the automatically selected regression model. Regression models numbered 2, 5, 6, 8, and 9 provided less precise annual sediment and phosphorus load estimates than the other regression models; however, these models were often selected by automatic model selection in LOADEST. Therefore, the annual pollutant load estimates for automatic model selection had less precision.

Pollutant regression models contain assumptions, and thus flow and water quality datasets need to match the assumptions to obtain accurate and precise pollutant load estimates. Sediment concentration

data in the study matched the assumptions of LOADEST, and thus LOADEST provided more accurate and more precise pollutant load estimates than LOADIN. On the other hand, nitrogen concentration data in the study displayed a poor relationship to streamflow data. Nitrogen concentration data did not match the assumptions of LOADEST. Therefore, LOADEST is better for pollutant load estimation when flow and concentration (or load) have a strong relationship.

Table 2. 95% Confidence Intervals of Estimated to Observed Pollutant Load Ratio for Annual Phosphorus Load Estimates by Fixed Sampling.

Model	95% Confidence Intervals of Ratios		
	Monthly fixed interval	Biweekly fixed interval	Weekly Fixed Interval
LD	0.791 ± 0.016	0.792 ± 0.026	0.767 ± 0.028
LT(1)	0.828 ± 0.011	0.837 ± 0.014	0.839 ± 0.016
LT(3)	0.842 ± 0.012	0.854 ± 0.014	0.858 ± 0.016
LT(4)	0.851 ± 0.012	0.863 ± 0.015	0.868 ± 0.016
LT(7)	0.872 ± 0.013	0.889 ± 0.015	0.898 ± 0.016

4. Conclusions

Both streamflow and water quality data are required to compute pollutant loads. However, water quality data are typically collected less frequently than streamflow, since it is costly to collect and to analyze water quality samples. Therefore, regression models are frequently used to estimate pollutant loads from limited water quality data. LOADEST and LOADIN were evaluated with subsampled water quality datasets from daily water quality data for nitrogen, phosphorus, and sediment.

Four distinct features were observed in the study. The first feature was that more frequent sampling frequencies did not necessarily lead to more accurate and more precise annual pollutant load estimates. The second feature was that supplementing fixed interval water quality data with water quality data collected from storm events improved both accuracy and precision in annual pollutant load estimates for all water quality parameters. The third feature was that the automatic model selection in LOADEST did not necessarily lead to more accurate and precise annual pollutant load estimates. The last feature was that the behaviors of regression models were different in annual pollutant load estimation for different water quality parameters.

The study indicates that regression models numbered 1, 3, 4, and 7 in LOADEST are more accurate and precise to annual phosphorus and sediment load estimation, that the sampling frequency for phosphorus and sediment needs to include storm samples, and that LOADIN is applicable to annual nitrogen load estimation.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Harmel, R.D.; King, K.W.; Haggard, B.E.; Wren, D.G.; Sheridan, J.M. Practical guidance for discharge and water quality data collection on small watershed. *Trans. Am. Soc. Agric. Eng.* **2006**, *49*, 937–948.
2. Halliday, S.J.; Skeffington, R.A.; Bowes, M.J.; Gozzard, E.; Newman, J.R.; Lowewenthal, M.; Palmer-Felgate, E.J.; Jarvie, H.P.; Wade, A.J. The water quality of the River Enborne, UK: Observations from high-frequency monitoring in a rural, lowland river system. *Water* **2014**, *6*, 150–180.
3. Sanders, E.C.; Yuan, Y.; Pitchford, A. Fecal coliform and *E. coli* concentrations in effluent-dominated streams of the Upper Santa Cruz watershed. *Water* **2013**, *5*, 243–261.
4. Valero, E. Characterization of the water quality status on a stretch of River Lerez around a small hydroelectric power station. *Water* **2012**, *4*, 815–834.
5. Robertson, D.M. Influence of different temporal sampling strategies on estimating total phosphorus and suspended sediment concentration and transport in small streams. *J. Am. Water Resour. Assoc.* **2003**, *39*, 1281–1308.
6. Gilroy, E.J.; Hirsch, R.M.; Cohn, T.A. Mean square error of regression-based constituent transport estimates. *Water Resour. Res.* **1990**, *26*, 2069–2077.
7. Johnson, A.H. Estimating solute transport in streams from grab samples. *Water Resour. Res.* **1979**, *15*, 1224–1228.
8. Horowitz, A.J. An evaluation of sediment rating curves for estimating suspended sediment concentrations for subsequent flux calculations. *Hydrol. Proc.* **2003**, *17*, 3387–3409.
9. Robertson, D.M.; Roerish, E.D. Influence of various water quality sampling strategies on load estimates for small streams. *Water Resour. Res.* **1999**, *35*, 3747–3759.
10. Henjum, M.B.; Hozalski, R.M.; Wennen, C.R.; Novak, P.J.; Arnold, W.A. A comparison of total maximum daily load (TMDL) calculations in urban streams using near real-time and periodic sampling data. *J. Environ. Monitor.* **2010**, *12*, 234–241.
11. Ullrich, A.; Volk, M. Influence of different nitrate-N monitoring strategies on load estimation as base for model calibration and evaluation. *Environ. Monit. Assess* **2010**, *171*, 513–527.
12. Toor, G.S.; Harmel, R.D.; Haggard, B.E.; Schmidt, G.S. Evaluation of regression methodology with low-frequency water quality sampling to estimate constituent loads for ephemeral watersheds in Texas. *J. Environ. Qual.* **2008**, *37*, 1847–1854.
13. Tesoriero, A.J.; Duff, J.H.; Wolock, D.M.; Spahr, N.E. Identifying pathways and processes affecting nitrate and orthophosphate inputs to streams in agricultural watersheds. *J. Environ. Qual.* **2009**, *38*, 1892–1900.
14. Runkel, R.L.; Crawford, C.G.; Cohn, T.A. *Load Estimator (LOADEST): A Fortran Program for Estimating Constituent Loads in Streams and Rivers*; U.S. Geological Survey Techniques and Methods: Reston, VA, USA, 2004.
15. Duan, S.; Kaushal, S.S.; Groffman, P.M.; Band, L.E.; Belt, K.T. Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed. *J. Geophys. Res.* **2012**, *117*, doi:10.1029/2011JG001782.

16. Brigham, M.E.; Wentz, D.A.; Aiken, G.R.; Krabbenhoft, D.P. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. *Environ. Sci. Technol.* **2009**, *43*, 2720–2725.
17. Dornblaser, M.M.; Striegl, R.G. Suspended sediment and carbonate transport in the Yukon River basin, Alaska: Fluxes and potential future responses to climate change. *Water Resour. Res.* **2009**, *45*, doi:10.1029/2008WR007546.
18. Oh, J.; Sankarasubramanian, A. Interannual hydroclimatic variability and its influence on winter nutrients variability over the southeast United States. *Hydrol. Earth Syst. Sci. Discuss.* **2011**, *8*, 10935–10971.
19. Park, Y.S.; Chaubey, I.; Lim, K.J.; Engel, B.A. Development of a web-based pollutant load interpolation tool using an optimization algorithm. In Proceedings of the American Society of Agricultural and Biological Engineers Annual International Meeting, Dallas, TX, USA, 29 July–1 August 2012.
20. National Center for Water Quality Research of Heidelberg University Homepage. Available online: <http://www.heidelberg.edu/academiclife/distinctive/ncwqr> (accessed on 23 March 2013).
21. USGS Water Quality Data for the Nation Homepage. Available online: <http://waterdata.usgs.gov/nwis/qw> (accessed on 23 March 2013).
22. Park, Y.S. Development and Enhancement of Web-Based Tools to Develop Total Maximum Daily Load. Ph.D. Thesis, Purdue University, West Lafayette, IN, USA, 18 May 2014; p. 19.
23. U.S. Environmental Protection Agency (USEPA). *An Approach for Using Load Duration Curves in the Development of TMDLs*; USEPA: Washington, DC, USA, 2007; p. 2.
24. Cohn, T.A.; Caulder, D.L.; Gilroy, E.J.; Zynjuk, L.D.; Summers, R.M. The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay. *Water Resour. Res.* **1992**, *28*, 2353–2463.
25. Powell, J.L. Least absolute deviations estimation for the censored regression model. *J. Economet.* **1984**, *25*, 303–325.
26. Phillips, J.M.; Webb, B.W.; Walling D.E.; Leeks, L. Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples. *Hydrol. Proc.* **1999**, *13*, 1035–1050.
27. Preston, S.D.; Bierman, V.J.; Silliman, S.E. An evaluation of methods for the estimation of tributary mass loads. *Water Resour. Res.* **1989**, *25*, 1379–1389.