Appendix 2. Model Archive Summary for Total Nitrogen at U.S. Geological Survey Station 06856600, Republican River at Clay Center, Kansas, during July 2018 through March 2021

This model archive summary summarizes the total nitrogen (TN) model developed to compute the 15-minute TN concentration from July 24, 2018, onward. This is the first model computing TN concentration that has been developed for this site. Model development was completed in accordance with Rasmussen and others (2009) and U.S. Geological Survey (2016).

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Site and Model Information

Station number: 06856600

Site name: Republican River at Clay Center, Kansas

Location: Latitude 39°21'20", longitude 97°07'38", referenced to North American Datum of 1927, in Clay County, Kansas, hydrologic unit code 10250017.

Water-quality equipment: A YSI, Inc., EXO3 water-quality monitor (YSI, Inc., 2017) equipped with sensors for water temperature, specific conductance, dissolved oxygen, pH, and turbidity was installed July 24, 2018. The EXO3 was housed in a 4-inch-diameter metal pipe suspended from the downstream side of the bridge in the deepest and fastest flowing water. Measurements from the EXO3 were recorded every 15 minutes and transmitted hourly via satellite.

Date model was created: August 23, 2021

Model calibration data period: August 1, 2018, through March 25, 2021 (dataset consisted of 42 discrete water-quality samples collected).

Model application date: July 24, 2018, onward (date of continuous water-quality monitor installation).

Total Nitrogen Concentration Data

Equal-width-increment samples (as described in U.S. Geological Survey, 2006) were collected from the downstream side of the bridge using a Federal Interagency Sedimentation Project US DH–95 depth-integrated sampler with a Teflon bottle, cap, and nozzle and a manually operated reel. Subsamples from 10 equally spaced verticals were composited. During July 2018 through June 2020, discrete water-quality samples were collected at Clay Center biweekly during May through October and monthly during November through April. During July 2020 through March 2021, discrete water-quality samples were collected about monthly. Samples were analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) in Lakewood, Colorado, in accordance with standard methods (Patton and Truitt, 2000; Patton and Kryskalla, 2011).

Continuous Water-Quality Data

Continuously measured (15-minute) water-quality data collection at Clay Center began on July 24, 2018. During July 2018 through March 2021, a YSI, Inc., EXO3 multiparameter sonde measured water temperature, specific conductance, pH, dissolved oxygen, and turbidity (YSI, Inc., 2017). The water-quality monitor was suspended from the bridge deck of Kansas Highway 18 near the centroid of flow. The continuous water-quality monitor was operated and maintained according to standard USGS methods (Wagner and others, 2006; Bennett and others, 2014). All continuous water-quality data at Clay Center are available in near-real time (updated hourly) from the USGS National Water Information System database (U.S. Geological Survey, 2021) using the station number 06856600.

Model Data

All data were collected using USGS protocols (U.S. Geological Survey, 2006; Wagner and others, 2006; Bennett and others, 2014) and are stored in the USGS National Water Information System database (U.S. Geological Survey, 2021). The regression model is based on 42 concurrent measurements of dissolved nitrate plus nitrite, total Kjeldahl nitrogen (TKN, also known as ammonia plus organic nitrogen), and continuously measured turbidity collected from August 1, 2018, through March 25, 2021. The potential explanatory variables

were interpolated from the continuous record and paired based on discrete sample collection time. Daylight saving time was observed, so sample time was either central standard time or central daylight time. The maximum time span between two continuous data points used for interpolation was 5 hours. Samples were collected throughout the range of continuously observed hydrologic conditions. Summary statistics and the complete model-calibration dataset are provided below.

TN was manually calculated as the sum of two components: dissolved nitrate plus nitrite (USGS parameter code 00631) and TKN (USGS parameter code 00625). The NWQL reporting limits were 0.01 milligram per liter (mg/L) as nitrogen for dissolved nitrate plus nitrite and 0.14 mg/L as nitrogen for TKN. Seven samples had censored (less than laboratory reporting limit) nitrate plus nitrite results (< 0.01 mg/L as nitrogen; data available in the Model-Calibration Datasets section of this appendix). No samples had censored TKN results. For all seven of the samples with censored nitrate plus nitrate results, the corresponding TKN result was greater than 1.0 mg/L as nitrogen and had only one decimal place. Therefore, the sum of TKN and dissolved nitrate plus nitrate was limited to one decimal place, and the censored nitrate plus nitrite result did not affect the sum calculation of TN. Thus, there were not any censored results in the TN dataset.

Potential outliers were identified as the data points for which both the studentized residual was greater than 3 or less than −3 and the Cook's D value exceeded the outlier test criteria, as described by Helsel and others (2020). This methodology resulted in zero potential outliers identified. All results were retained in the model calibration dataset.

Model Development

All continuously measured water-quality parameters and streamflow were considered as explanatory variables for estimating TN concentration using ordinary least squares regression. All models that predict TN and logarithm base 10 TN ($\log_{10}$[TN]) were evaluated from simple linear regression (SLR; single explanatory variable) and multiple linear regression (more than one explanatory variable) models. Potential regression models were evaluated based on normality and homoscedasticity in residual values. Residual values are the difference between the measured and predicted values. Homoscedastic plots are those in which the magnitude

of residual values does not change substantially over the range of predicted values; that is, the magnitude of residual values neither increases nor decreases over the range of predicted values and the variance is constant. These comparisons led to the conclusion that the most appropriate and reliable model would be the SLR that estimated the $\log_{10}$(TN).

Turbidity was selected as the best predictor of TN in an SLR model transformed by $\log_{10}$ based on residual plots, fairly high adjusted coefficient of determination (R^2_{adj}) compared to other models considered, and fairly low model standard percentage error compared to other models considered. Additional explanatory variables in multiple linear regression models did not substantially increase the R^2_{adj} value. Values for the aforementioned statistics and metrics were computed and are included below along with all relevant sample data and more indepth statistical information.

Model Summary

Summary of final regression analysis for TN at U.S. Geological Survey station 06856600.

TN concentration model:

$$log_{10}(TN) = 0.344 \times log_{10}(TBY) - 0.258,$$

where

TN = total nitrogen, calculated as the sum of dissolved nitrate plus nitrite and total Kjeldahl nitrogen, in milligrams per liter as nitrogen, and

TBY = turbidity, YSI EXO3, in formazin nephelometric units.

Turbidity makes physical and statistical sense as an explanatory variable for TN. Turbidity makes sense physically because suspended solids (including some with attached nitrogen) in the water column scatter light and increase turbidity. The model selected was the simplest model (one explanatory variable) and the best statistically.

The $\log_{10}$-transformed model may be retransformed to the original units so that TN can be calculated directly. The retransformation introduces a negative bias in the retransformed calculated constituent (Helsel and others, 2020). This bias may be corrected using Duan's bias correction factor (BCF; Duan, 1983; Helsel and others, 2020). For this model, the calculated BCF was 1.04. The retransformed model, accounting for BCF, is as follows:

$$TN = 0.574 \times TBY^{0.344}.$$

Total Nitrogen Concentration Record

The TN concentration record is computed using this regression model and stored at the National Real-Time Water Quality website. Model-estimated concentrations in the National Real-Time Water Quality website are computed at hourly intervals. The complete water-quality record is available at https://nrtwq.usgs.gov/ks.

Remarks

All regression models were developed using R software environment (R Core Team, 2021).

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Model Statistics, Data, and Plots

Definitions for terms used in this output are provided at the end of this document.

Model

log*TN*=+0.344×log*TBY*−0.258

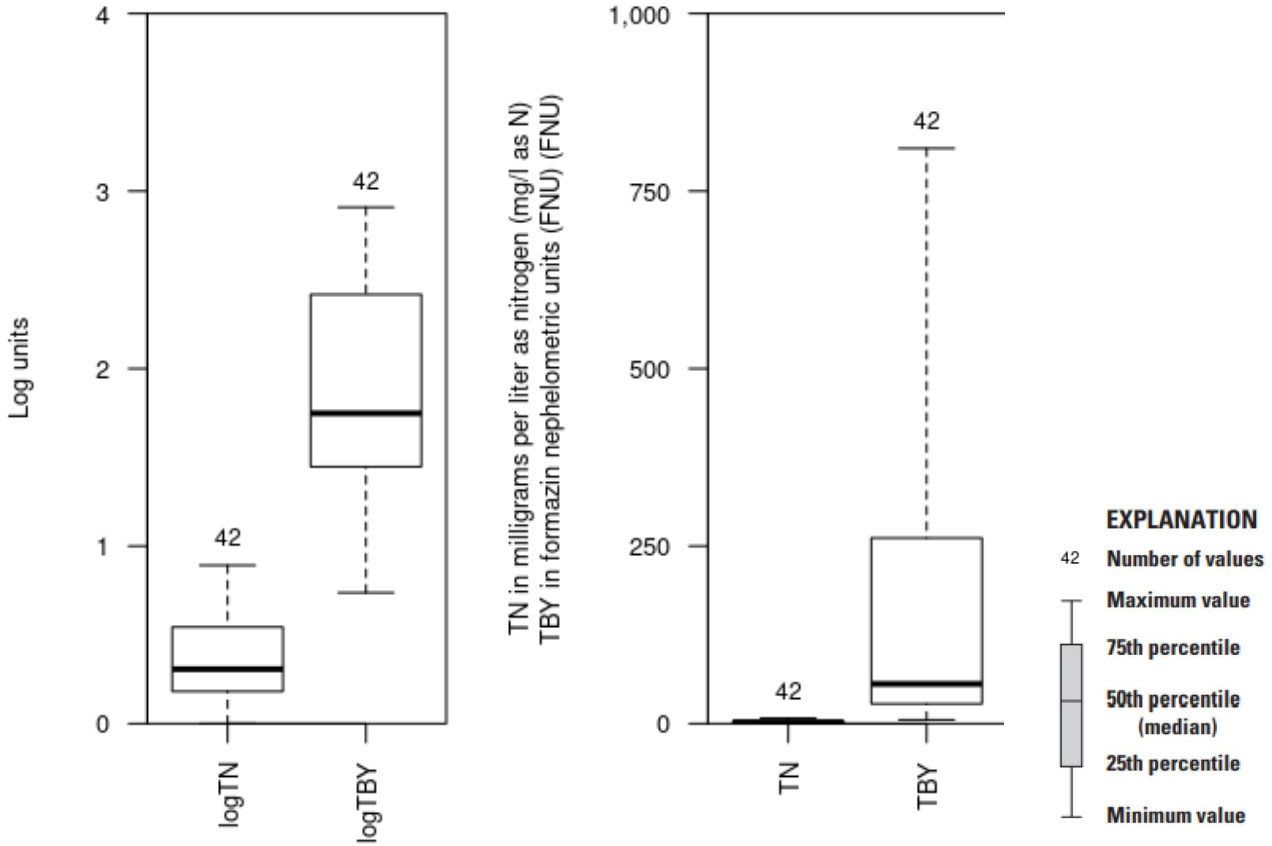
Variable Summary Statistics

```
               logTN   TN logTBY    TBY
Minimum        0.000 1.00  0.738   5.47
First Quartile 0.182 1.52  1.450  28.00
```

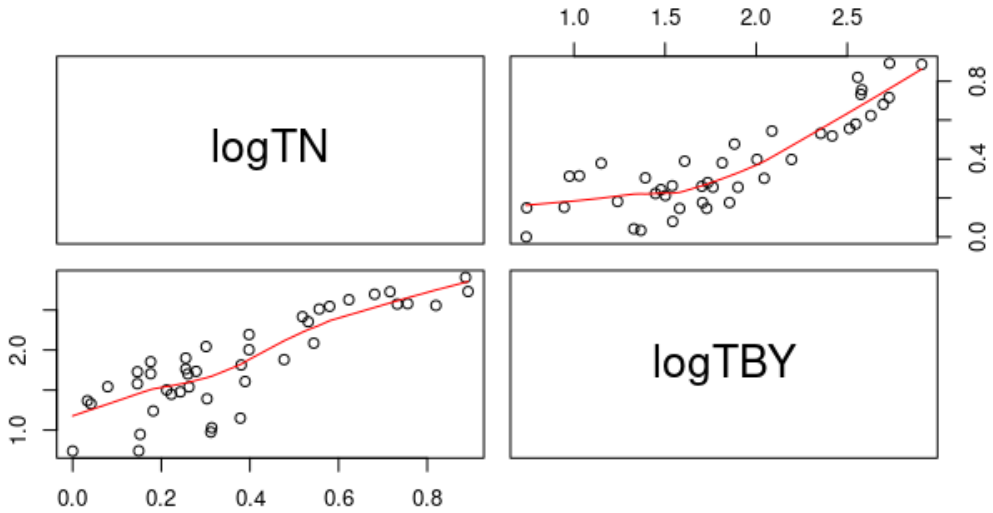
Median	0.307	2.03	1.750	56.00
Mean	0.375	2.79	1.840	155.00
Third Quartile	0.544	3.50	2.420	261.00
Maximum	0.892	7.80	2.910	810.00

TN cannot be extrapolated more than 10 percent outside the range of sample data used to fit the model (U.S. Geological Survey, 2016). Because the maximum observed continuous turbidity value in the calibration dataset was 810 formazin nephelometric units (FNU), the maximum turbidity value for which this model is valid is 891 FNU. Less than 1 percent (59 of 84,392 15-minute measurements) of continuous turbidity measurements during the study period exceeded 891 FNU. Accounting for the BCF, at a turbidity of 891 FNU, the model-estimated TN value is 5.9 mg/L as nitrogen.

Box Plots

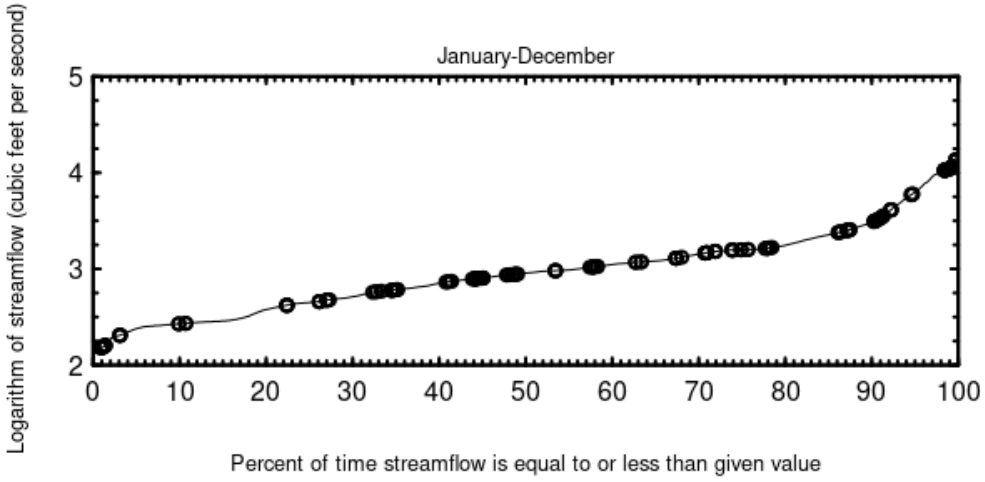


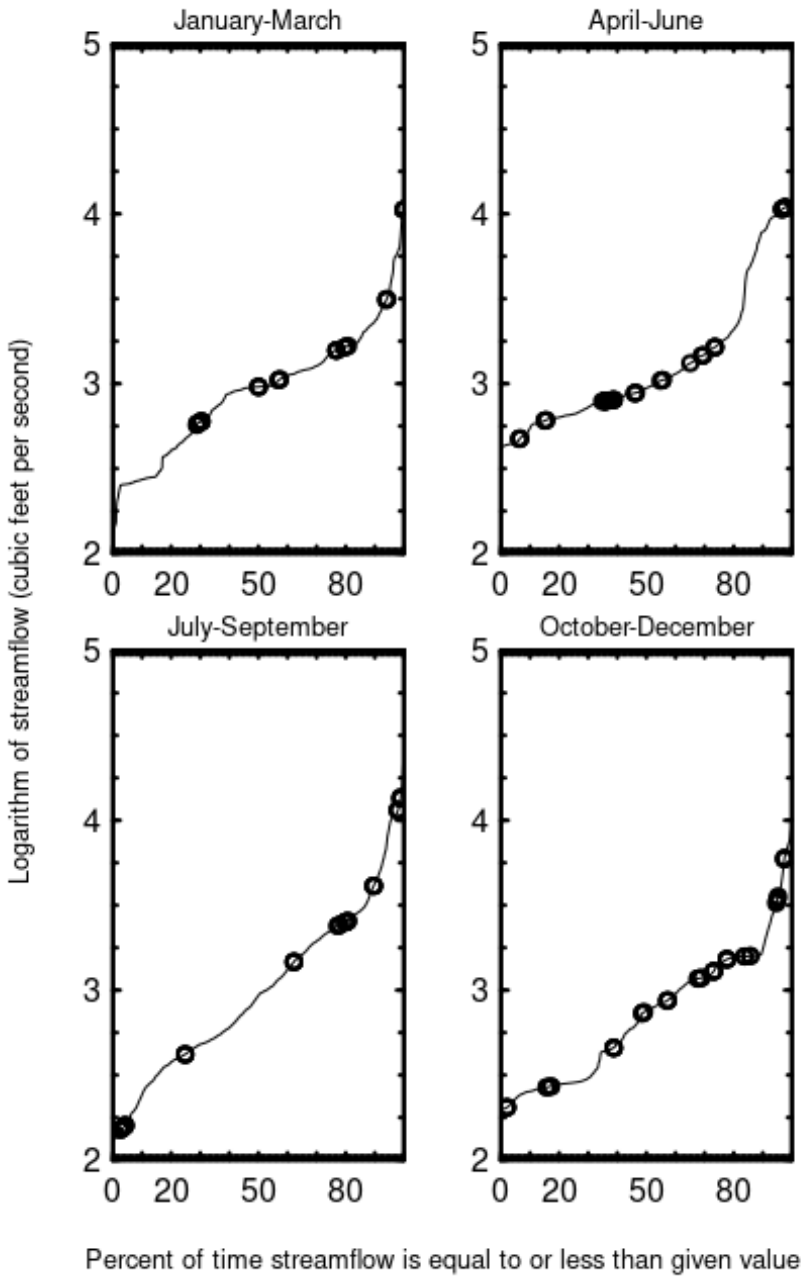
Exploratory Plots



Red lines show the locally weighted scatterplot smoothing (Cleveland, 1979; Helsel and others, 2020).

The x- and y-axis labels for a given bivariate plot are defined by the intersecting row and column labels.





Basic Model Statistics

Number of observations	42
Standard error (root mean square error [RMSE])	0.127
Average model standard percentage error (MSPE)	29.7
Coefficient of determination (R^2)	0.726
Adjusted coefficient of determination (R^2_{adj})	0.719
Bias correction factor (BCF)	1.04

Explanatory Variables

	Coefficients	Standard Error	t value	$Pr(>\|t\|)$
(Intercept)	−0.258	0.0647	−3.99	2.70e−04
logTBY	0.344	0.0335	10.30	8.59e−13

Correlation Matrix

	Intercept	E.vars
Intercept	1.000	−0.953
E.vars	−0.953	1.000

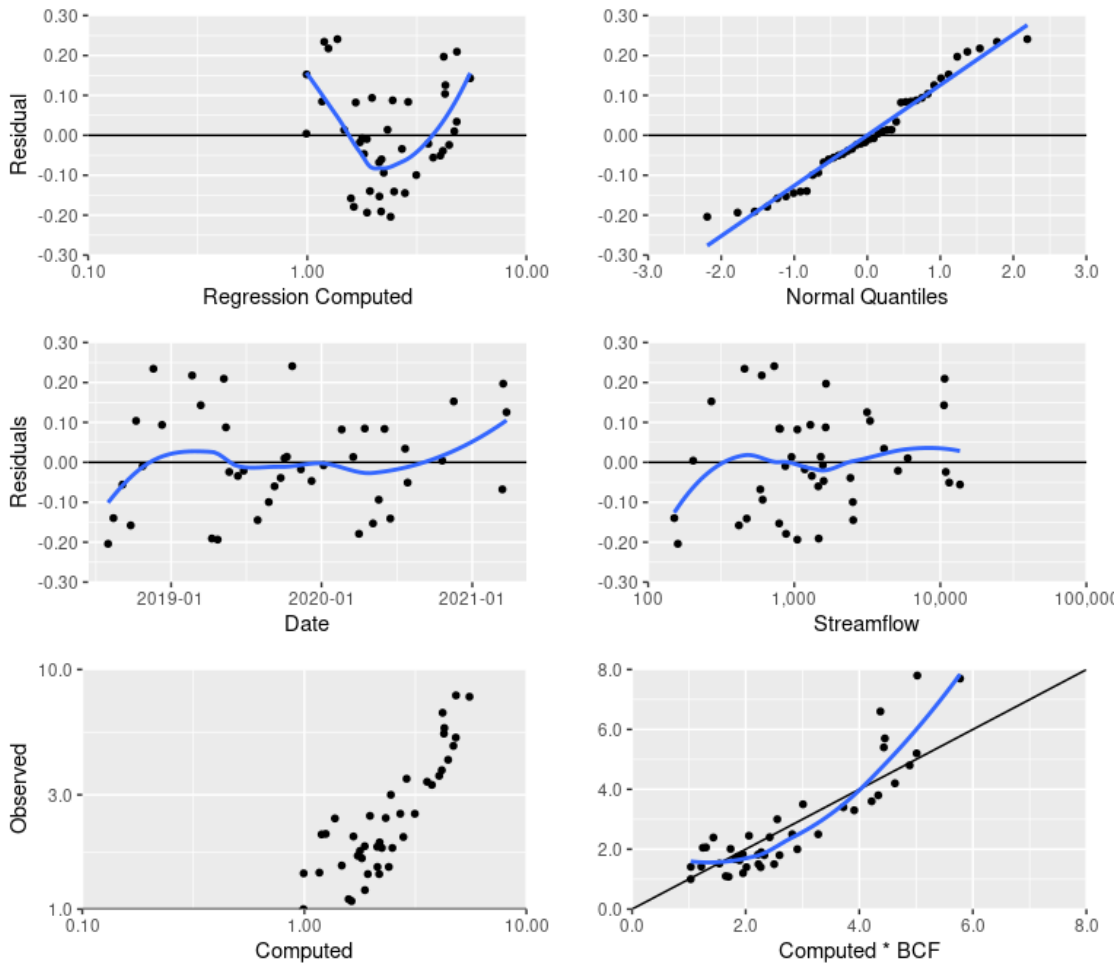
Outlier Test Criteria

Leverage	Cook's D	DFFITS
0.143	0.194	0.436

Flagged Observations

	logTN	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
11/19/2018 13:10	0.312	0.07750	0.234	1.92	1.98	0.0756	0.150	0.568
2/21/2019 12:30	0.314	0.09630	0.218	1.77	1.82	0.0693	0.117	0.498
5/9/2019 10:20	0.892	0.68300	0.209	1.71	1.76	0.0791	0.126	0.515
10/22/2019 11:40	0.378	0.13800	0.241	1.95	2.02	0.0568	0.114	0.497
11/17/2020 11:10	0.149	−0.00325	0.152	1.27	1.28	0.1080	0.097	0.444

Statistical Plots



First row (left): residual TN (in log-space units) related to regression-computed TN (in milligrams per liter as nitrogen) with local polynomial regression fitting, or locally estimated scatterplot smoothing (LOESS), indicated by the blue line.

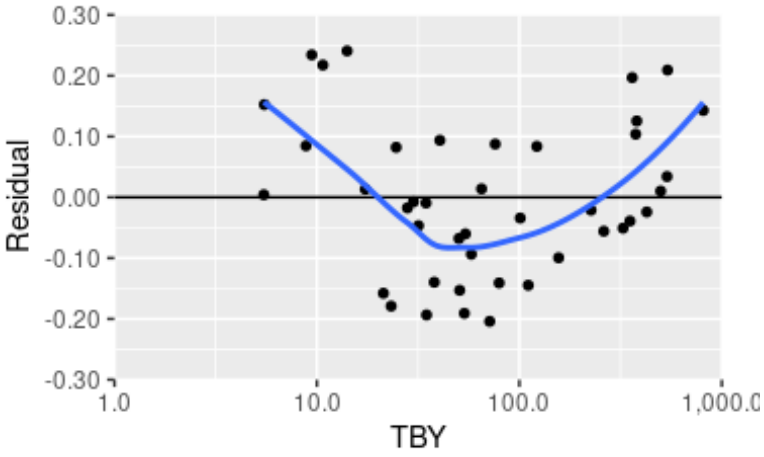
First row (right): residual TN (in log-space units) related to the corresponding normal quantile (unitless) of the residual with simple linear regression indicated by the blue line.

Second row (left): residual TN (in log-space units) related to date with LOESS indicated by the blue line.

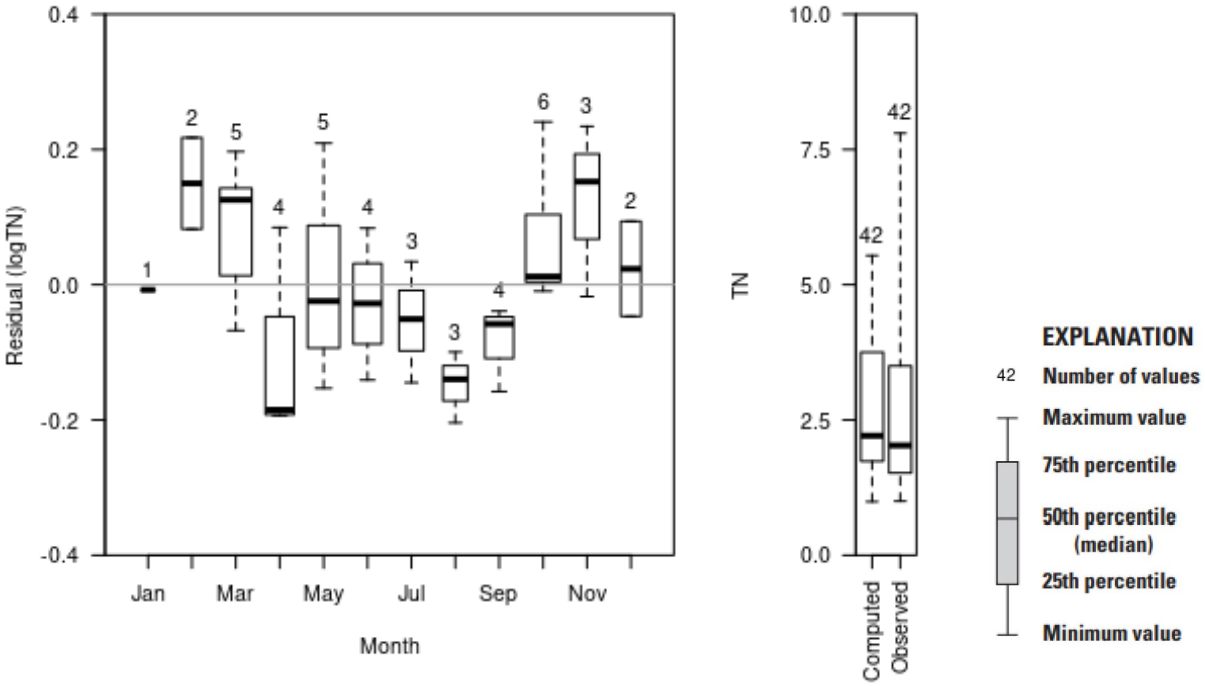
Second row (right): residual TN (in log-space units) related to streamflow (in cubic feet per second) with LOESS indicated by the blue line.

Third row (left): observed TN (in milligrams per liter as nitrogen) related to regression-computed TN (in milligrams per liter as nitrogen).

Third row (right): observed TN (in milligrams per liter as nitrogen) related to the product of regression-computed TN (in milligrams per liter as nitrogen) and the BCF with LOESS indicated by the blue line.

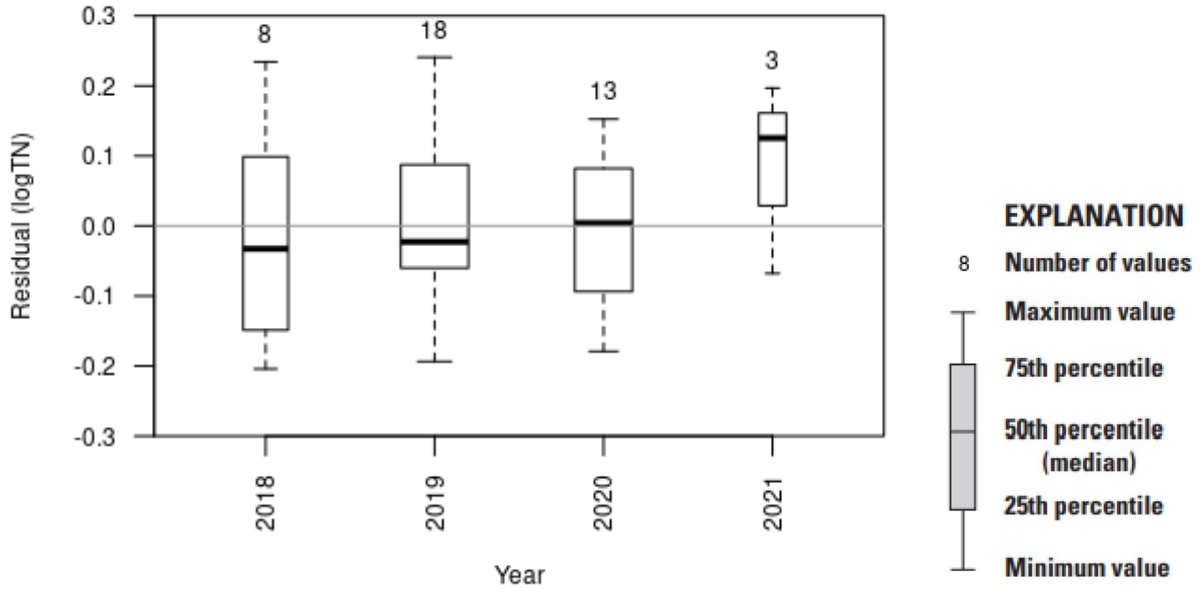


Residual TN (in log-space units) related to TBY (in formazin nephelometric units) with LOESS indicated by the blue line.



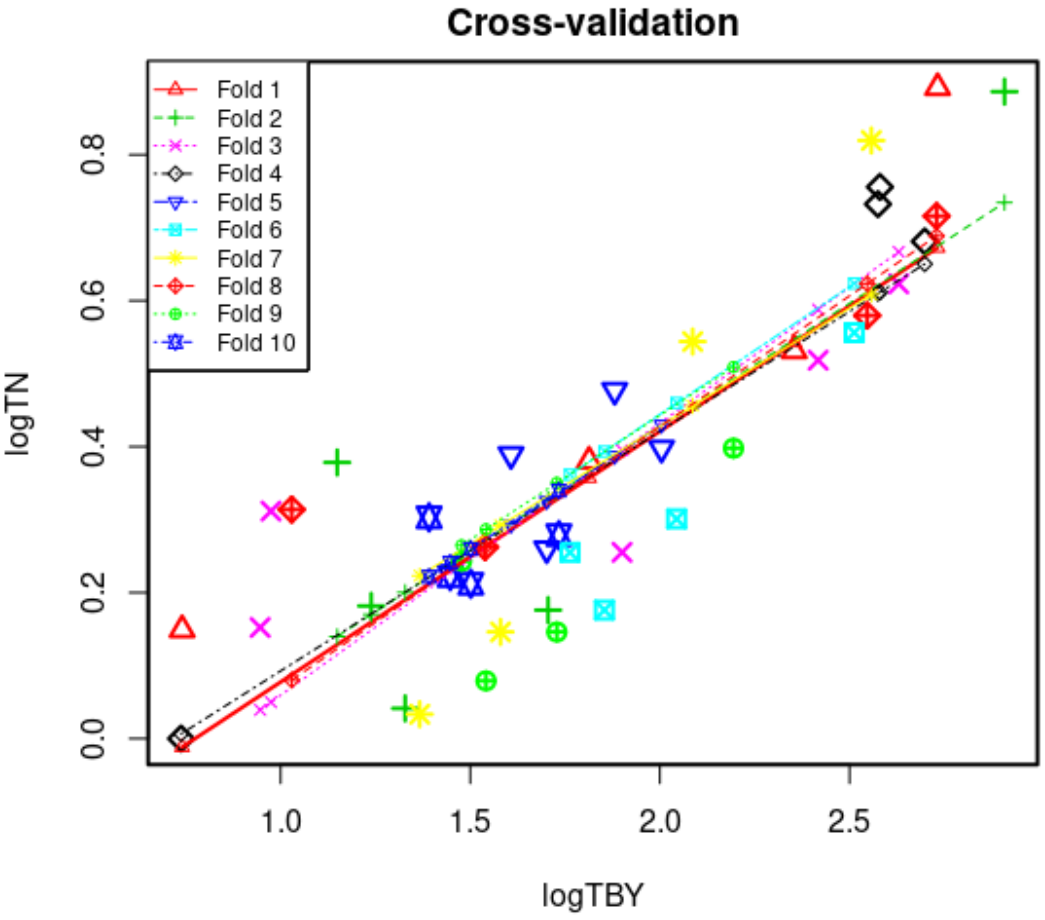
Left: residual TN (in log-space units) by month.

Right: TN (in milligrams per liter as nitrogen) in regression-computed and observed values.



Residual TN (in log-space units) by year.

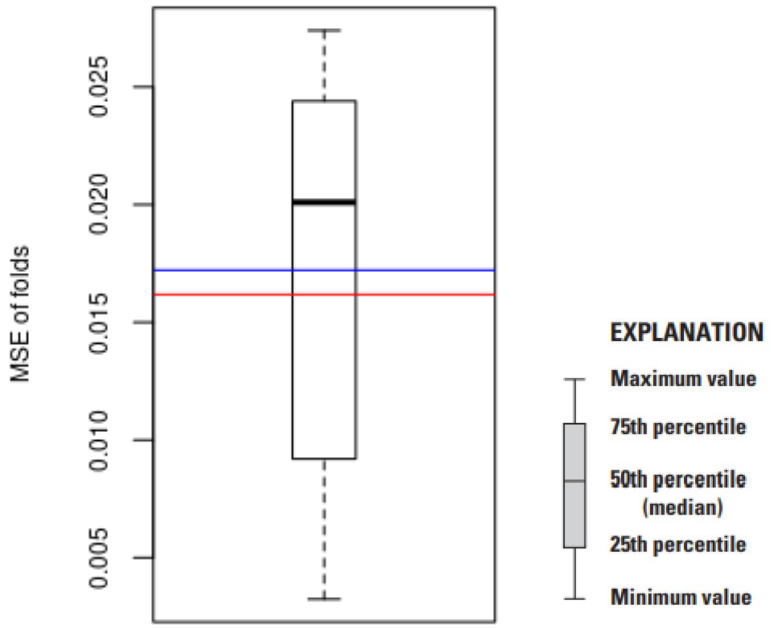
Cross Validation



TN (in log-space units) related to TBY (in log-space units) for 10 folds of data. Each fold is an equal partition of the data (10 percent of the data). Large symbols are the observed values of data points removed in a fold and

small symbols are the recomputed values of data points removed in a fold. Recomputed regression lines are adjusted regression lines with one fold removed.

```
              Minimum MSE of folds:  0.00324
                 Mean MSE of folds:  0.01720
               Median MSE of folds:  0.02010
              Maximum MSE of folds:  0.02740
(Mean MSE of folds) / (Model MSE):  1.06000     (MSE ratio)
```




```
Red line - Model MSE (unitless)
Blue line - Mean MSE of folds (unitless)
```

Model-Calibration Datasets

Total nitrogen was manually computed by adding total Kjeldahl nitrogen (TKN, USGS parameter code 00625, also known as total ammonia plus organic nitrogen) and dissolved nitrate (NO3) plus nitrite (NO2) (USGS parameter code 00631).

	Date	TKN	NO3+NO2	TN
1	2018-08-01	1.5	< 0.01	1.5
2	2018-08-14	1.4	< 0.01	1.4
3	2018-09-05	2.8	0.5	3.3
4	2018-09-25	1.1	< 0.01	1.1
5	2018-10-08	3.0	2.35	5.4
6	2018-10-24	0.98	0.85	1.83
7	2018-11-19	0.54	1.51	2.05
8	2018-12-10	0.89	1.56	2.45
9	2019-02-21	0.49	1.57	2.06
10	2019-03-14	6.5	1.24	7.7

11	2019-04-10	1.4	< 0.01	1.4
12	2019-04-24	1.2	< 0.01	1.2
13	2019-05-09	5.0	2.79	7.8
14	2019-05-14	1.3	1.68	3.0
15	2019-05-22	2.2	1.95	4.2
16	2019-06-12	1.5	0.99	2.5
17	2019-06-26	1.9	1.52	3.4
18	2019-07-30	1.1	0.86	2.0
19	2019-08-26	1.4	1.06	2.5
20	2019-09-09	1.2	0.73	1.9
21	2019-09-24	2.5	1.30	3.8
22	2019-10-03	3.6	1.16	4.8
23	2019-10-09	1.1	1.25	2.4
24	2019-10-22	0.66	1.73	2.39
25	2019-11-12	0.73	0.94	1.67
26	2019-12-08	0.71	0.92	1.63
27	2020-01-06	0.72	1.03	1.75
28	2020-02-19	0.70	1.31	2.01
29	2020-03-18	0.84	0.68	1.52
30	2020-04-01	0.88	0.20	1.08
31	2020-04-15	0.61	0.81	1.42
32	2020-05-05	1.3	0.21	1.5
33	2020-05-19	1.8	< 0.01	1.8
34	2020-06-02	1.6	1.92	3.5
35	2020-06-16	1.8	< 0.01	1.8
36	2020-07-22	3.9	1.28	5.2
37	2020-07-28	2.8	0.79	3.6
38	2020-10-20	0.52	0.48	1.00
39	2020-11-17	0.52	0.89	1.41
40	2021-03-15	0.96	0.86	1.82
41	2021-03-17	4.3	2.32	6.6
42	2021-03-25	3.7	1.98	5.7

The manual TN sum was then used in the model-calibration dataset.

	Date	logTN	logTBY	TN	TBY	Computed logTN	Computed TN	Residual	Normal Quantiles	Censored Values
1	2018-08-01	0.176	1.85	1.5	71.4	0.38	2.5	−0.204	−2.19	--
2	2018-08-14	0.146	1.58	1.4	38	0.286	2.01	−0.14	−0.828	--
3	2018-09-05	0.519	2.42	3.3	261	0.574	3.91	−0.0558	−0.461	--
4	2018-09-25	0.0414	1.33	1.1	21.3	0.199	1.65	−0.158	−1.23	--
5	2018-10-08	0.732	2.57	5.4	376	0.629	4.43	0.104	0.828	--
6	2018-10-24	0.262	1.54	1.83	34.6	0.272	1.95	−0.0094	0.0297	--
7	2018-11-19	0.312	0.975	2.05	9.43	0.0775	1.25	0.234	1.78	--
8	2018-12-10	0.389	1.61	2.45	40.5	0.295	2.06	0.0938	0.747	--
9	2019-02-21	0.314	1.03	2.06	10.7	0.0963	1.3	0.218	1.54	--
10	2019-03-14	0.886	2.91	7.7	810	0.744	5.78	0.143	1.01	--
11	2019-04-10	0.146	1.73	1.4	53.5	0.337	2.27	−0.191	−1.54	--
12	2019-04-24	0.0792	1.54	1.2	34.8	0.273	1.95	−0.194	−1.78	--
13	2019-05-09	0.892	2.73	7.8	540	0.683	5.02	0.209	1.37	--
14	2019-05-14	0.477	1.88	3	76	0.39	2.56	0.0876	0.671	--
15	2019-05-22	0.623	2.63	4.2	426	0.647	4.63	−0.0242	−0.149	--

16	2019-06-12	0.398	2	2.5	101	0.432	2.82	−0.0342	−0.209	--
17	2019-06-26	0.531	2.35	3.4	226	0.553	3.72	−0.0211	−0.0892	--
18	2019-07-30	0.301	2.04	2	111	0.446	2.91	−0.145	−1.01	--
19	2019-08-26	0.398	2.19	2.5	156	0.497	3.28	−0.0995	−0.747	--
20	2019-09-09	0.279	1.73	1.9	54.2	0.339	2.27	−0.0601	−0.528	--
21	2019-09-24	0.58	2.55	3.8	352	0.619	4.33	−0.0391	−0.271	--
22	2019-10-03	0.681	2.7	4.8	499	0.671	4.89	0.0102	0.209	--
23	2019-10-09	0.38	1.81	2.4	65.1	0.366	2.42	0.0139	0.333	--
24	2019-10-22	0.378	1.15	2.39	14.1	0.138	1.43	0.241	2.19	--
25	2019-11-12	0.223	1.45	1.67	28	0.24	1.81	−0.0175	−0.0297	--
26	2019-12-08	0.212	1.5	1.63	31.7	0.259	1.89	−0.0467	−0.333	--
27	2020-01-06	0.243	1.48	1.75	30	0.251	1.86	−0.00748	0.0892	--
28	2020-02-19	0.303	1.39	2.01	24.6	0.221	1.73	0.0822	0.461	--
29	2020-03-18	0.182	1.24	1.52	17.3	0.168	1.54	0.0134	0.271	--
30	2020-04-01	0.0334	1.37	1.08	23.3	0.212	1.7	−0.179	−1.37	--
31	2020-04-15	0.152	0.946	1.42	8.83	0.0676	1.22	0.0847	0.598	--
32	2020-05-05	0.176	1.71	1.5	50.7	0.329	2.22	−0.153	−1.11	--
33	2020-05-19	0.255	1.76	1.8	57.9	0.349	2.33	−0.0937	−0.671	--
34	2020-06-02	0.544	2.09	3.5	122	0.46	3.01	0.0837	0.528	--
35	2020-06-16	0.255	1.9	1.8	79.5	0.396	2.6	−0.141	−0.915	--
36	2020-07-22	0.716	2.73	5.2	536	0.682	5.01	0.0341	0.396	--
37	2020-07-28	0.556	2.51	3.6	325	0.607	4.22	−0.0508	−0.396	--
38	2020-10-20	0	0.738	1	5.47	-0.00416	1.03	0.00416	0.149	--
39	2020-11-17	0.149	0.74	1.41	5.5	-0.00325	1.03	0.152	1.11	--
40	2021-03-15	0.26	1.7	1.82	50.3	0.328	2.22	−0.0678	−0.598	--
41	2021-03-17	0.82	2.56	6.6	361	0.623	4.37	0.197	1.23	--
42	2021-03-25	0.756	2.58	5.7	380	0.63	4.45	0.125	0.915	--

Definitions

Cook’s D: Cook’s distance, a measure of influence (Helsel and others, 2020).

DFFITS: difference in fits, a measure of influence (Helsel and others, 2020).

E.vars: explanatory variables.

Leverage: a data point’s distance from the middle (mean) value in the x direction (Helsel and others, 2020).

LOESS: local polynomial regression fitting, or locally estimated scatterplot smoothing (Helsel and others, 2020).

LOWESS: locally weighted scatterplot smoothing (Cleveland, 1979; Helsel and others, 2020).

Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen mg/L–N) (U.S. Geological Survey parameter code 00631) (U.S. Geological Survey method code RED02).

MSE: model standard error, also known as standard error of the regression (Helsel and others, 2020).

MSPE: model standard percentage error (Helsel and others, 2020).

$Pr(>|t|)$: probability that the independent variable has no effect on the dependent variable (Helsel and others, 2020).

RMSE: root mean square error (Helsel and others, 2020).

t value: Student's t value; the coefficient divided by its associated standard error (Helsel and others, 2020).

TBY: Turbidity, water, unfiltered, monochrome near infrared light-emitting diode, 780–900 nm, detection angle 90±2.5 degrees, in formazin nephelometric units (U.S. Geological Survey parameter code 63680) (U.S. Geological Survey method code TS213).

TKN: total Kjeldahl nitrogen, also known as ammonia plus organic nitrogen, water, unfiltered, in milligrams per liter as nitrogen (U.S. Geological Survey parameter code 00625) (U.S. Geological Survey method code KJ008).

TN: total nitrogen, calculated as the sum of total Kjeldahl nitrogen (U.S. Geological Survey parameter code 00625, also known as total ammonia plus organic nitrogen) and dissolved nitrate plus nitrite (U.S. Geological Survey parameter code 00631), in milligrams per liter as nitrogen.

App Version 1.0

References Cited

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