Appendix 9. Model Archive Summary for Nitrate at U.S. Geological Survey Site 07144780, North Fork Ninnescah River above Cheney Reservoir, Kansas, during January 1, 1999, through December 31, 2019

This model archive summary summarizes the nitrate (NO_3) model developed to compute hourly or daily nitrate concentrations during January 1, 1999, onward. This model supersedes all prior models used during this period. The methods used follow U.S. Geological Survey (USGS) guidance as referenced in relevant Office of Surface Water/Office of Water Quality Technical Memoranda and USGS Techniques and Methods, book 3, chapter C4 (Rasmussen and others, 2009).

Site and Model Information

Site number: 07144780

Site name: North Fork Ninnescah River above Cheney Reservoir, Kansas

Location: Lat 37°51'45", long 98°00'49" referenced to North American Datum of 1927, in NE 1/4 SE 1/4 NE 1/4 sec.19, T.25 S., R.6 W., Reno County, Kans., Hydrologic Unit 11030014, on right bank at upstream side of county highway bridge, 10 miles south of Hutchinson, 18.1 miles upstream from Cheney Dam.

Equipment: A YSI 6600 Extended Deployment System water-quality monitor equipped with sensors for water temperature, specific conductance, pH, dissolved oxygen, and turbidity (a YSI Model 6026 turbidity sensor [November 9, 1998, to December 1, 2010] and a YSI Model 6136 turbidity sensor [October 17, 2009, to November 12, 2015; March 31, 2017, to June 7, 2017]) (YSI Incorporated, 2007, 2012a). The YSI 6600 water-quality monitor was in operation during November 9, 1998, through November 12, 2015.

A Xylem YSI EXO2 water-quality monitor equipped with sensors for water temperature, specific conductance, dissolved oxygen, pH, and turbidity (YSI Incorporated, 2012b). The YSI EXO2 water-quality monitor began operation on November 13, 2015. Monitors were housed in a 4-inch diameter polyvinyl chloride (PVC) pipe and placed in a location representative of the stream cross section. Monitor readings were recorded and satellite transmitted hourly.

Date model was developed: April 26, 2019

Model calibration data period: January 26, 1999, to September 28, 2017

Model Data

All data were collected using USGS protocols (U.S. Geological Survey, 2006; Wagner and others, 2006; Sauer and Turnipseed, 2010; Turnipseed and Sauer, 2010) and are stored in the National Water Information System (NWIS) database (https://doi.org/10.5066/F7P55KJN; U.S. Geological Survey, 2020). Explanatory variables were evaluated individually and in combination. Potential explanatory variables included streamflow, water temperature, specific conductance, pH, dissolved oxygen, and turbidity. Seasonal components (sine and cosine variables) were also evaluated as explanatory variables.

The regression model is based on 109 concomitant values of discretely collected nitrate samples and continuously measured specific conductance during January 26, 1999, through September 28, 2017. Discrete samples were collected over a range of streamflows. One sample was less than the minimum reporting level (less than [<] 0.01 milligram per liter); therefore, a Tobit regression model was developed to compute estimates of nitrate using the absolute maximum likelihood estimation and approach (Hald, 1949; Cohen, 1950; Tobin, 1958; Helsel and others, 2020). Summary statistics and the complete model-calibration data are provided below. Potential outliers were identified using the methods described in Rasmussen and others (2009). Additionally, outlier test criteria, including leverage and Cook's distance (Cook's D), were used to estimate potential outlier influence on the final Tobit regression model (Cook, 1977). The sample collected on March 22, 2006, had a large specific conductance value likely from previous road salt application and was removed from the model calibration dataset. Previous

outliers (Stone and others, 2013) were examined and retained in the dataset if there were no clear issues, explanations, or conditions that would cause a result to be invalid for model calibration.

Nitrate

Discrete samples were collected from the downstream side of the bridge or instream within 50 feet of the bridge using equal-width-increment, multiple vertical, single vertical, or grab methods following U.S. Geological Survey (2006) and Rasmussen and others (2014). Discrete samples were collected on a semifixed to event-based schedule ranging from 2 to 17 samples per year with a Federal Interagency Sedimentation Project U.S. DH–95 or D–95 with a Teflon bottle, cap, and nozzle depth-integrating sampler; a DH–81 with a Teflon bottle, cap, and nozzle hand sampler; or a grab sample with a Teflon bottle depending on sample location. Samples were analyzed for nitrate by the Wichita Municipal Water and Wastewater Laboratory in Wichita, Kans., according to standard methods (American Public Health Association and others, 1995).

Continuous Data

Specific conductance was measured with a YSI 6600 sensor during November 9, 1998, through November 12, 2015, and a YSI EXO2 sensor during November 13, 2015, through December 31, 2019. Concomitant specific conductance values were time interpolated. If continuous data were not available (2 or more hours of specific conductance values bracketing the sample collection time were missing) because of fouling, changes in equipment, or unsuitable site conditions, then the field monitor specific conductance value measured during sampling was substituted. If no concomitant continuous data were available, the sample was not included in the dataset.

Model Development

Stepwise regression analysis was done using R programming language (R Core Team, 2019) to relate discretely collected nitrate to specific conductance and other continuously measured data. The distribution of residuals was examined for normality and plots of residuals (the difference between the measured and model calculated values) compared to model calculated nitrate were examined for homoscedasticity (departures from zero did not change substantially over the range of model calculated values).

About 1 percent of the model-calibration dataset consisted of censored results (less than minimum reporting level). Tobit regression models were developed using absolute maximum likelihood estimation methods using the *smwrQW* (v.0.7.9) package in R programming language (R Core Team, 2019).

Specific conductance and seasonality were selected as best predictors of nitrate based on residual plots, a higher pseudocoefficient of determination (pseudo- R^2), and relatively low estimated standard residual error (RSE). Seasonality was included as an explanatory variable because nitrate seems to have a cyclical pattern potentially influenced by groundwater during low seasonal flow.

Model Summary

Summary of final nitrate regression analysis at USGS site 07144780:

Nitrate-based model:

```
NO3 = 0.00037 \times SPC + 0.0265 \times \sin(2\pi D) + 0.538 \times \cos(2\pi D) + 0.532,
```

where,

NO3 = nitrate, filtered, in milligrams per liter as nitrogen; SPC = specific conductance, in microsiemens per centimeter at 25 degrees Celsius; and D = date, in decimal years.

Previous Models

Version	Model Equation	Reference
1.0	$NO3 = -0.389 \times \log_{10}(TBY6026) + 0.0519 \times \sin(2\pi D) + 0.619 \times \cos(2\pi D) + 1.63$	Stone and others (2013)

Model Statistics, Plots and Data

Definitions for terms used in this output can be found at the end of this document.

Model

```
NO3 = 0.00037 \times SPC + 0.0265 \times \sin(2\pi D) + 0.538 \times \cos(2\pi D) + 0.532
```

Computation method: Absolute Maximum Likelihood Estimation (AMLE)

Explanatory Variables

```
Coefficients:

Estimate Std. Error z-score p-value

(Intercent) 0 5324600 8 7670-02 6 0736 0 0000
```

```
(Intercept) 0.5324609 8.767e-02 6.0736 0.0000 SPC 0.0003698 8.572e-05 4.3141 0.0000 sin2piD 0.0264661 3.955e-02 0.6692 0.4943 cos2piD 0.5381386 5.703e-02 9.4362 0.0000
```

Basic Model Statistics

For a detailed definition and explanation of the terms used below, refer to Helsel and others (2020).

```
Estimated residual standard error (Unbiased) = 0.2947

Number of observations = 109, number censored = 1 (0.9 percent)

Log-likelihood (model) = -20.56

Log-likelihood (intercept only) = -68.16

Chi-square = 95.19

degrees of freedom = 3

p-value = <0.0001

Computation method: AMLE

Pseudo-R-squared: 0.5832

Akaike Information Criterion: 51.12

Bayesian Information Criterion: 64.57

Variance inflation factors

SPC 1.08

sin2piD 1.03

cos2piD 1.11
```

Outlier Test Criteria

```
leverage cooksD
0.08257 0.84457
```

Flagged Observations

```
Observations exceeding at least one test criterion
Nitrate ycen yhat resids leverage cooksD

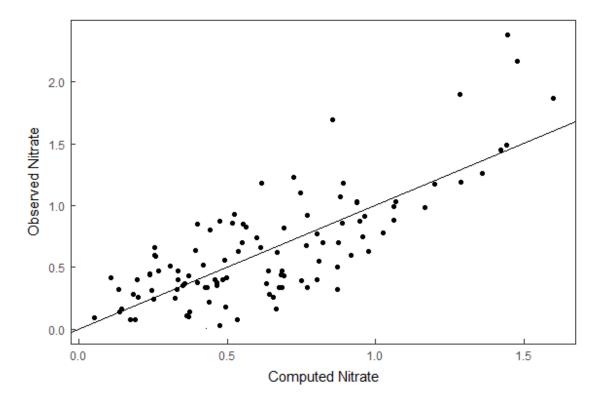
26  0.32 FALSE 0.8712 -0.5512  0.09838  0.10587

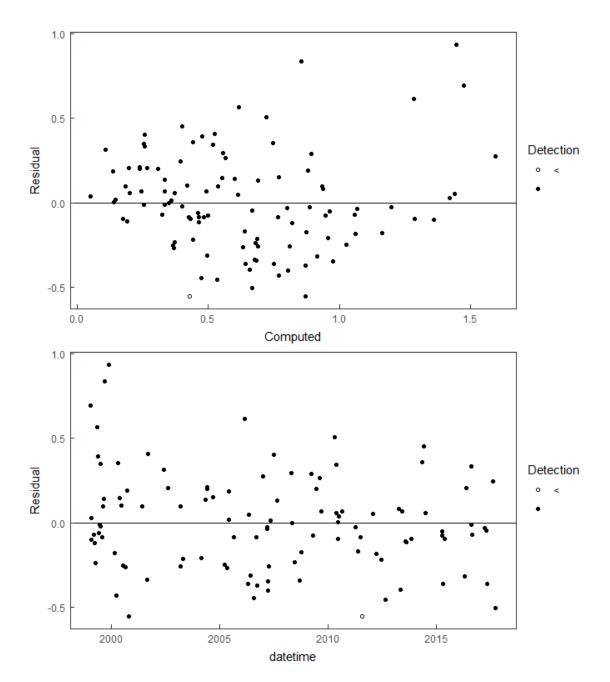
53  1.87 FALSE 1.5970  0.2730  0.08530  0.02187
```

95% Confidence Intervals

	2.5 %	97.5 %
(Intercept) 0.3606352627	0.7042865690
SPC	0.0002017926	0.0005378037
sin2piD	-0.0510453473	0.1039776464
cos2piD	0.4263633220	0.6499138899

Plots





Variable Summary Statistics

Independent Variable (xvar) - Specific Conductance

Min. 1st Qu. Median Mean 3d Qu. Max. 156.5 559.0 897.0 849.1 1,153.5 1,432.5

Standard Deviation

[1] 347.8235

Dependent Variable (yvar) - Nitrate

Min. 1st Qu. Median Mean 3d Qu. Max. <0.01 0.34 0.5 0.6333 0.86 2.38

Standard Deviation

[1] 0.4497

Model Calibration Dataset

1999-01-26 11:50:00 2.17 21:00 21999-01-31 14:25:00 1.16 11:44 1.4767 0.6994A7 1999-01-31 14:25:00 1.45 11:44 1.4224 0.027787 1999-02-30 10:45:00 1.45 11:44 1.4224 0.027787 1999-03-17 11:40:00 0.99 979 1.6599 0.069706 1.999-04-16 12:55:00 0.44 697 0.6807 0.240591 1999-05-24 10:45:00 0.44 697 0.6807 0.240591 1999-05-24 10:45:00 0.87 590 0.4761 0.394164 1999-05-24 10:45:00 0.87 590 0.4761 0.394164 1999-05-24 10:45:00 0.87 590 0.4761 0.394164 1999-06-25 10:15:00 0.4 133 0.4596 0.087 0.323 0.012074 11:1999-07-02 10:15:00 0.67 705 0.2549 0.3323 0.012074 11:1999-07-02 10:15:00 0.67 705 0.2549 0.345270 1999-07-14 11:20:00 0.83 1147 0.4657 0.085472 1.999-07-14 11:20:00 0.83 1147 0.4657 0.085468 1.999-08-22 11:20:00 0.74 10:31 0.690 0.74 10:31 0.999-07-29 09:55:00 0.74 10:31 0.999-08-26 10:55:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:50:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:35:00 0.74 10:31 0.999-08-26 10:30:00 0.74 10:31 0.999-08-26 10:30:00 0.74 10:31 0.999-08-26 10:30:00 0.74 10:31 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26 10:30:00 0.999-08-26	IVIOC	del Calibration Dataset				
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	2016-04-19 10:25:00	0.6 1432	0.9169 -0.316603
	2016-05-25 10:10:00	0.4 225	0.1961 0.203993
	2016-08-07 12:30:00	0.59 464	0.2584 0.331729
	2016-08-13 11:30:00	0.24 361	0.2539 -0.013757
	2016-08-27 09:20:00	0.25 292	0.3230 -0.072965
	2017-03-29 10:45:00	0.77 576	0.8021 -0.031981
	2017-04-20 12:00:00	0.62 762	0.6688 -0.048654
107	2017-05-02 09:50:00	0.28 972	0.6430 -0.362825

108 2017-08-11 11:00:00	0.64 789	0.3948 0.245352
109 2017-09-28 10:30:00	0.16 502	0.6664 -0.506328

Definitions

NO3: nitrate, filtered, in milligrams per liter as nitrogen (00618)

SPC: specific conductance, in microsiemens per centimeter at 25 degrees Celsius (00095)

D: date, in decimal years

Leverage: an outlier's measure in the x-direction (Helsel and others, 2020).

p-value: the probability that the independent variable has no effect on the dependent variable (Helsel and others, 2020).

Pseudo-R-squared: pseudocoefficient of determination. An estimation of the proportion of variance in the response variable explained by the model (McKelvey and Zavoina, 1975).

z-score: the estimated coefficient divided by its associated standard error (Helsel and others, 2020).

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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