Appendix 21. Model Archival Summary for Nitrate + Nitrite Concentration at Station 06887500; Kansas River at Wamego, Kansas

This model archival summary summarizes the nitrate + nitrite concentration (NO_x) model developed to compute 15-minute NO_x from July 19, 2012 onward. This model supersedes all previous models.

Site and Model Information

Site number: 06887500
Site name: Kansas River at Wamego, Kansas
Location: Lat 39°11'54", long 96°18'19" referenced to North American Datum of 1927, in SW 1/4 NW 1/4 SE 1/4 sec.9, T.10 S., R.10 E., Pottawatomie County, KS, Hydrologic Unit 10270102.

Equipment: An YSI 6600 water-quality monitor equipped with sensors for water temperature, specific conductance, dissolved oxygen, pH, turbidity, and chlorophyll was installed from August 2012 through May 2014. From June 2014 to the present (2015) a Xylem YSI EXO2 water-quality monitor equipped was installed with sensors for water temperature, specific conductance, dissolved oxygen, pH, turbidity, and chlorophyll. The monitor is housed in a 4-inch diameter galvanized steel pipe. Readings from the water-quality monitor are recorded every 15 minutes and transmits data by way of satellite, hourly.

Date model was created: October 15, 2015

Model calibration data period: July 19, 2012 – June 29, 2015

Model application date: July 19, 2012 onward

Model-Calibration Dataset

All data were collected using U.S. Geological Survey (USGS) protocols and are stored in the National Water Information System (NWIS) database. Linear regression models were developed using the open-source software package "R." Explanatory variables selected as inputs to linear regression were physicochemical properties: specific conductance, pH, water temperature, dissolved oxygen, turbidity, chlorophyll fluorescence, and streamflow. Seasonal components (sine and cosine variables) were also evaluated as explanatory variables in the models to determine if seasonal changes affected the model. All combinations of physicochemical properties and a seasonal component were evaluated to determine which combinations produced the best models.

The final selected regression model is based on 54 concurrent measurements of NO_x concentration, specific conductance (SC), and chlorophyll (Chl) collected from July 19, 2012 through June 29, 2015. Samples were collected throughout the range of continuously observed hydrologic conditions. Three samples were below laboratory detection limits; two samples were below 0.04 and one sample was below 0.01. Summary statistics and the complete model-calibration dataset are provided below. Studentized residuals from the final model were inspected for values greater than 3 or less than negative 3. Values outside of that range are considered potential outliers and are investigated. None of the NO_x samples were deemed outliers.

Nitrate + Nitrite Sampling Details

Cross-section samples are typically collected either from the downstream side of the bridge or instream within 100 feet of the bridge. The equal-width-increment (EWI) method is used, and samples typically are composited for analysis. Cross-section samples are collected every 2 weeks from March through October, once a month from November through February, and during selected runoff events. A FISP US DH-95, D-95, or D-96A1 depth integrating sampler is used from the bridge; and a DH-81 or DH-95 hand sampler is used for boat samples. Samples are analyzed for NO_x concentration at the USGS National Water Quality Laboratory in Lakewood, Colorado.

Model Development

Regression analysis was done using R by examining SC, Chl, streamflow, and other continuously measured data as explanatory variables for estimating NO_x concentration. A variety of models that predict NO_x, $(NO_x)^2$, $\sqrt{NO_x}$ and models that predict $\log_{10}(NO_x)$ were evaluated. The distribution of residuals was examined for normality, and plots of residuals (the difference between the measured and computed values) as compared to computed NO_x were examined for homoscedasticity (meaning that their departures from zero

did not change substantially over the range of computed values). This comparison lead to the conclusion that the most appropriate and reliable model would be one that estimated NO_x.

SC and Chl were selected as the best predictors of NO_x based on residual plots, relatively high adjusted coefficient of determination (adjusted R^2) and relatively low model standard percentage error (*MSPE*), prediction error sum of squares (PRESS), and Mallow's C_p. Values for all of the afore mentioned statistics and metrics were computed for various models and are included below along with all relevant sample data and more in-depth statistical information.

Model Summary

Summary of final regression analysis for NO_x concentration at site number 06887500.

NO_x concentration-based model:

$$NO_x = -0.00102 \times SC - 0.0176 \times Chl + 1.85$$

where

NO_x = inorganic nitrogen (nitrate and nitrite) in milligrams per liter as N (mg/L);

SC = specific conductance in microsiemens per centimeter at 25 degrees Celsius (µs/cm); and,

Chl = chlorophyll in micrograms per liter (µg/L)

SC and Chl make physical and statistical sense as explanatory variables for NO_x.

Previous Models

Start year	End year	Model
2000	2005	$NO_x = 1.09 \times \log_{10}(Q) - 0.397 \times \log_{10}(WT) - 2.53$

Nitrate + Nitrite Concentration Record

The NO_x record is computed using this regression model and stored at the National Real-Time Water Quality (NRTWQ) Web site. Data are computed at 15-minute intervals. The complete water-quality record can be found at http://nrtwq.usgs.gov/ks.

Remarks

None

R Output for Nitrate + Nitrite 06887500; Kansas River at Wamego, KS

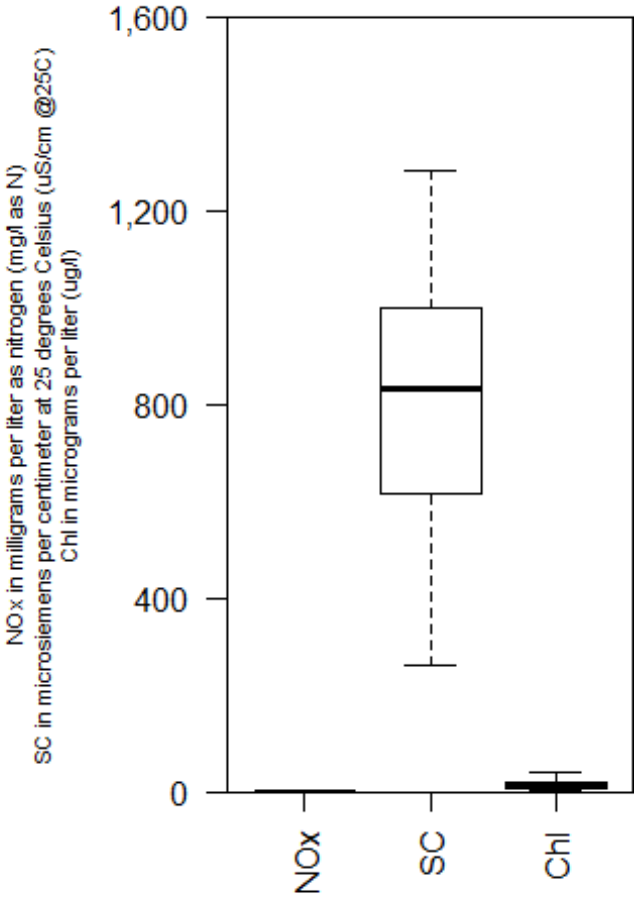
Model Form

NOx = + -0.00102 * SC + -0.0176 * Chl + 1.85

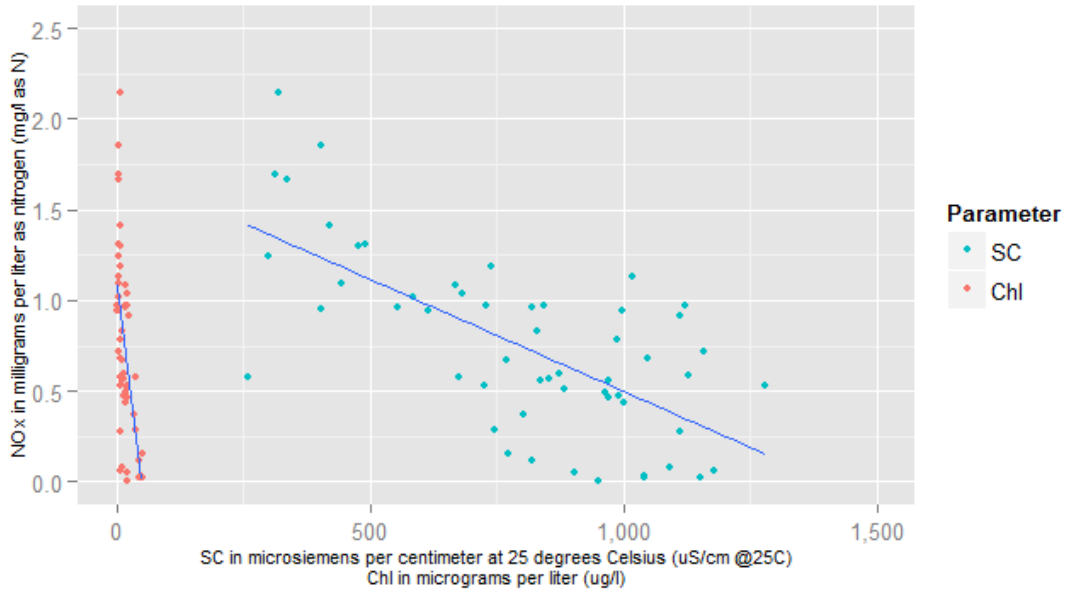
Variable Summary Statistics

	NOx	SC	Chl
Minimum	0.005	260	1.7
1st Quartile	0.466	616	6.13
Median	0.671	833	11.6
Mean	0.748	800	16.4
3rd Quartile	1.01	1000	21.3
Maximum	2.15	1280	51.2
Censored [< 0.01]	1	--	--
Censored [< 0.04]	2	--	--

Box Plot(s) of sample data



Exploratory Plot



Model Calibration

Basic Data

Number of Observations	54
Standard error (RMSE)	0.29
Upper Model standard percentage error (MSPE)	38.8
Lower Model standard percentage error (MSPE)	38.8
Coefficient of determination (R^2)	0.667
Adjusted Coefficient of Determination (Adj. R^2)	0.654

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Variance Inflation Factors (VIF)
      SC      Chl
1.068078 1.068078
```

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(>|t|)
(Intercept)	1.85000	0.126000	14.60	6.75e-20
SC	-0.00102	0.000153	-6.64	2.00e-08
Chl	-0.01760	0.003080	-5.71	5.86e-07

Correlation Matrix

	Intercept	SC	Chl
Intercept	1.000	-0.868	-0.156
SC	-0.868	1.000	-0.252
Chl	-0.156	-0.252	1.000

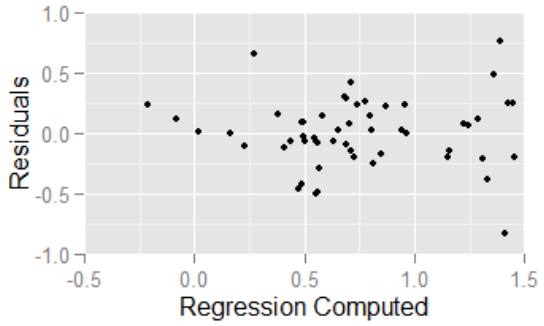
Test Criteria

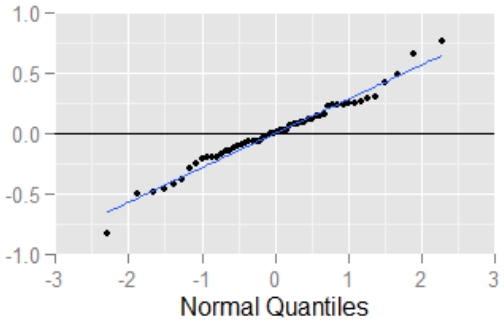
```
 Leverage  Cook's D    DFFITS
0.1111111 0.1940305 0.3849002
```

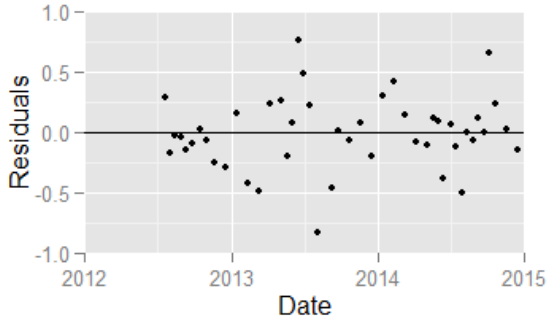
Flagged Observations

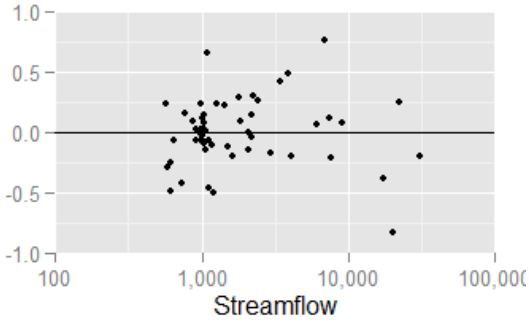
	NOx	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
2/11/2013 8:20	0.06111	0.48870	-0.427600	-1.5310	-1.55200	0.07223	6.082e-02	-0.43300
3/11/2013 9:00	0.07732	0.56250	-0.485100	-1.7180	-1.75200	0.05131	5.320e-02	-0.40750
4/8/2013 7:40	0.02000	-0.21270	0.232700	0.8713	0.86920	0.15190	4.533e-02	0.36790
6/17/2013 8:30	2.14500	1.38600	0.759300	2.7290	2.92400	0.07916	2.134e-01	0.85730
7/1/2013 8:10	1.85000	1.36100	0.489200	1.7450	1.78200	0.06493	7.047e-02	0.46950
8/5/2013 7:30	0.57520	1.41000	-0.834300	-3.0240	-3.30500	0.09447	3.180e-01	-1.06800
5/19/2014 8:00	0.03338	-0.08116	0.114500	0.4253	0.42180	0.13700	9.571e-03	0.16810
8/11/2014 9:20	0.15650	0.16320	-0.006678	-0.0251	-0.02485	0.15820	3.946e-05	-0.01077
10/6/2014 9:00	0.91780	0.26790	0.649800	2.2960	2.40100	0.04694	8.653e-02	0.53280

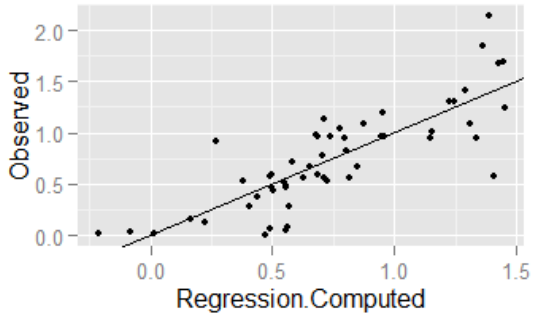
Statistical Plots

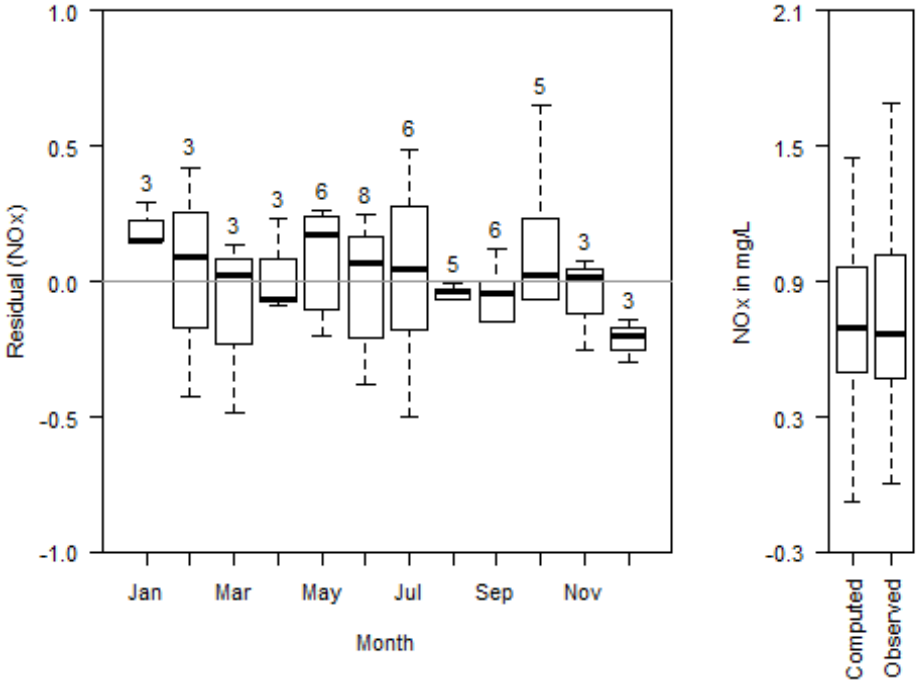




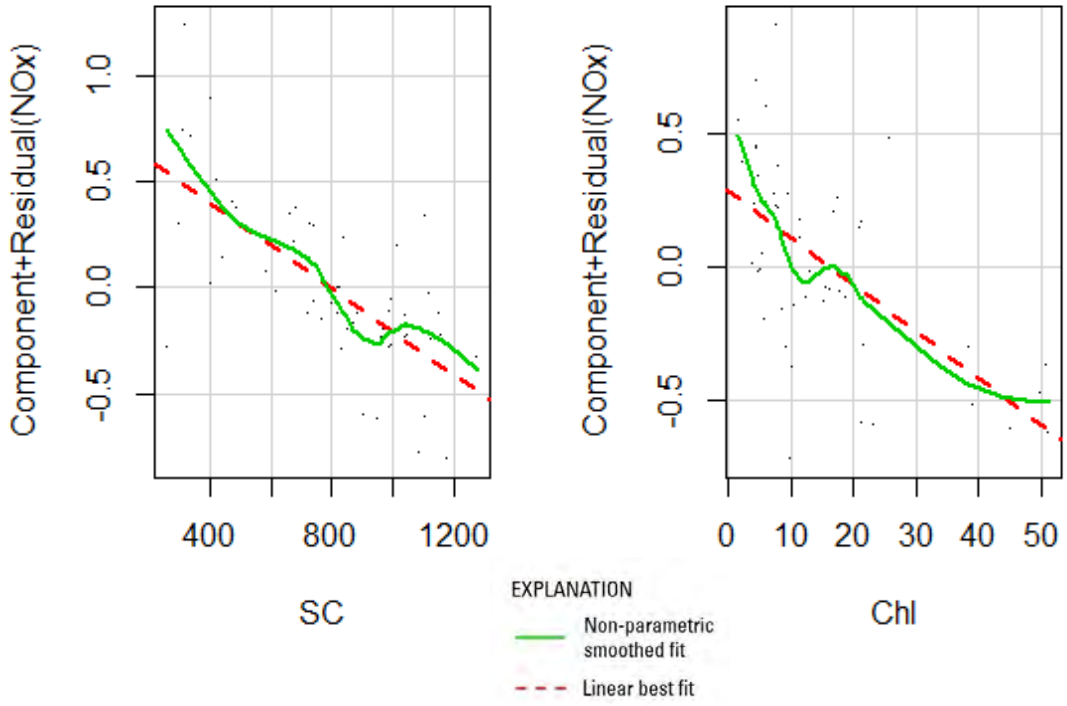








Component + Residual Plots



Models considered

Model Formula	Number of Variables	Standard Error	R2	Adjusted R2	Cp	PRESS	VIF	MSPE
NOx ~ logSC	1	0.3623	47.06	46.04	36.77	7.709	1	48
NOx ~ logQ	1	0.3676	45.51	44.46	39.31	7.742	1	49
NOx ~ SC	1	0.3676	45.5	44.45	39.32	7.727	1	49
NOx ~ SC + logChl	2	0.2844	68	66.74	4.454	4.691	1.071	38
NOx ~ SC + Chl	2	0.2899	66.75	65.44	6.505	4.882	1.068	39
NOx ~ logSC + logChl	2	0.2921	66.26	64.94	7.3	5.102	1.11	39
NOx ~ Q + logSC + logChl	3	0.2756	70.55	68.78	2.269	4.641	2.984	37
NOx ~ Q + SC + logChl	3	0.2794	69.73	67.91	3.619	4.665	2.235	37
NOx ~ Q + logSC + Chl	3	0.2847	68.56	66.67	5.53	4.976	2.898	38
NOx ~ Q + logQ + logSC + logChl	4	0.2731	71.66	69.35	2.449	4.683	5.089	37
NOx ~ Q + logSC + logChl + cos2DY	4	0.2743	71.4	69.07	2.877	4.699	2.994	37
NOx ~ Q + logQ + logSC + Chl	4	0.2758	71.09	68.73	3.39	4.798	5.078	37
NOx ~ Q + logQ + logSC + Chl + logChl	5	0.2733	72.19	69.3	3.574	4.704	5.091	37
NOx ~ Q + logQ + logSC + logChl + cos2DY	5	0.2744	71.98	69.06	3.93	4.877	5.329	37
NOx ~ Q + logQ + logSC + logChl + sin2DY	5	0.2756	71.72	68.77	4.353	4.86	5.099	37
NOx ~ Q + logQ + logSC + Chl + logChl + cos2DY	6	0.2749	72.45	68.93	5.153	4.92	5.338	37
NOx ~ Q + logQ + logSC + Chl + logChl + sin2DY	6	0.2755	72.33	68.8	5.35	4.856	5.104	37
NOx ~ Q + logQ + SC + logSC + Chl + logChl	6	0.2761	72.2	68.65	5.56	5.72	7.681	37

Data

	Date	NOx	SC	Chl	Computed NOx	Residual	Normal Quantiles	Censored Values
1	2012-07-19	0.9678	842	17.4	0.6877	0.28	1.26	--
2	2012-07-30	0.6665	770	12.5	0.8469	-0.18	-0.731	--
3	2012-08-13	0.4665	970	21	0.4944	-0.0279	-0.116	--
4	2012-08-27	0.5094	884	22.9	0.5483	-0.0389	-0.163	--
5	2012-09-10	0.5673	854	15.3	0.7124	-0.145	-0.672	--
6	2012-09-24	0.5946	872.3	15.65	0.6876	-0.093	-0.455	--
7	2012-10-15	0.8305	828.7	11.57	0.8037	0.0268	0.163	--
8	2012-10-29	0.561	970.5	13.25	0.6302	-0.0692	-0.305	--
9	2012-11-19	0.5625	837	10.53	0.8135	-0.251	-1.08	--
10	2012-12-17	0.2749	1110	8.6	0.5703	-0.295	-1.17	--
11	2013-01-14	0.5319	1280	9.68	0.3787	0.153	0.672	--
12	2013-02-11	0.06111	1180	9.2	0.4887	-0.428	-1.37	--
13	2013-03-11	0.07732	1090	10.2	0.5625	-0.485	-1.66	--
14	2013-04-08	0.02	1151	50.77	-0.2127	0.233	0.858	< 0.04
15	2013-05-06	1.04	682	21.4	0.7798	0.26	1.17	--
16	2013-05-20	0.5266	726	21.8	0.7281	-0.201	-0.793	--
17	2013-06-03	1.303	476.6	7.84	1.227	0.0759	0.305	--
18	2013-06-17	2.145	320.3	7.8	1.386	0.759	2.29	--
19	2013-07-01	1.85	404	4.4	1.361	0.489	1.66	--
20	2013-07-15	1.088	667.5	16.95	0.8727	0.215	0.731	--
21	2013-08-05	0.5752	259.8	9.96	1.41	-0.834	-2.29	--
22	2013-09-09	0.005	952	23.2	0.474	-0.469	-1.5	< 0.01
23	2013-09-23	0.02	1040	44.2	0.01552	0.00448	0.0231	< 0.04
24	2013-10-21	0.4332	1000	18.8	0.5026	-0.0694	-0.354	--
25	2013-11-18	0.7795	987.2	8	0.7055	0.074	0.257	--
26	2013-12-16	0.9472	616.3	4.07	1.151	-0.204	-0.858	--
27	2014-01-13	0.9746	1120	1.7	0.6814	0.293	1.37	--
28	2014-02-10	1.133	1017	6	0.7104	0.422	1.5	--
29	2014-03-10	0.7202	1160	4.93	0.584	0.136	0.56	--
30	2014-04-07	0.471	991.4	16.11	0.5587	-0.0877	-0.404	--

31	2014-05-05	0.1205	818.7	45.09	0.2245	-0.104	-0.506	--
32	2014-05-19	0.03338	1040	49.7	-0.08116	0.115	0.455	--
33	2014-06-02	0.575	675.1	38.4	0.4879	0.0871	0.354	--
34	2014-06-11	0.954	404	5.9	1.334	-0.38	-1.26	--
35	2014-06-30	1.307	490.3	6.13	1.243	0.0638	0.21	--
36	2014-07-14	0.2856	744.4	39.08	0.4056	-0.12	-0.56	--
37	2014-07-28	0.05441	905	21.3	0.5551	-0.501	-1.89	--
38	2014-08-11	0.1565	773	51.22	0.1632	-0.00668	-0.0694	--
39	2014-08-25	0.3688	803	33.88	0.4375	-0.0688	-0.257	--
40	2014-09-08	1.41	420.2	7.55	1.289	0.121	0.506	--
41	2014-09-22	0.9603	553.3	18.53	0.9609	-0.000576	-0.0231	--
42	2014-10-06	0.9178	1110	25.8	0.2679	0.65	1.89	--
43	2014-10-20	1.189	740	8.12	0.9543	0.234	0.926	--
44	2014-11-17	0.9629	818.5	4.2	0.9436	0.0194	0.0694	--
45	2014-12-15	1.014	585.2	5.5	1.158	-0.144	-0.615	--
46	2015-01-12	0.9413	996.7	2.37	0.7948	0.146	0.615	--
47	2015-02-09	0.5868	1130	11.55	0.4981	0.0887	0.404	--
48	2015-03-09	0.6764	1048	7.52	0.6522	0.0242	0.116	--
49	2015-04-06	0.491	965.5	17.8	0.5553	-0.0643	-0.21	--
50	2015-05-04	0.9706	728	20.96	0.7408	0.23	0.793	--
51	2015-05-18	1.668	336	4.58	1.427	0.241	1	--
52	2015-06-01	1.093	445.5	4.95	1.309	-0.216	-1	--
53	2015-06-15	1.695	313.3	4.68	1.448	0.247	1.08	--
54	2015-06-29	1.245	300	5.28	1.451	-0.206	-0.926	--

Definitions and National Water Information System (parameter code)

NOx: Inorganic nitrogen (nitrate and nitrite) in mg/L as N (00631)
SC: Specific conductance in uS/cm @25C (00095)
Chl: in ug/L (32318)