

Appendix 4. Model Archival Summary for Calcium Concentration at U.S. Geological Survey Site 06892350, Kansas River at De Soto, Kansas, during July 2012 through September 2019

This model archival summary summarizes the calcium (Ca; U.S. Geological Survey [USGS] parameter code 00915) concentration model developed to compute 15-minute Ca concentrations from July 2012 onward. This model supersedes all previous models.

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Site and Model Information

Site number: 06892350

Site name: Kansas River at De Soto, Kansas

Location: Lat 38°59'00", long 94°57'52" referenced to North American Datum of 1927, in NE 1/4 SE 1/4 SE 1/4 sec.28, T.12 S., R.22 E., Leavenworth County, Kans., hydrologic unit 10270104.

Equipment: A YSI 6600 water-quality monitor equipped with sensors for water temperature, specific conductance (SC), dissolved oxygen, pH, and turbidity was installed from August 2012 through June 2014. A Xylem YSI EXO2 water-quality monitor equipped with sensors for water temperature, SC, dissolved oxygen, pH, turbidity, and chlorophyll and phycocyanin fluorescence was installed during June 2014 through September 2019. A Hach Nitratax plus sc sensor (5-millimeter path length) that monitors ultraviolet (UV) nitrate concentrations was installed from June 2013 through September 2019. The monitors were housed in side-by-side 4-inch-diameter galvanized steel pipes. Readings from the water-quality and nitrate plus nitrite monitors were recorded every 15 minutes and transmitted by way of satellite, hourly.

Date model was created: March 27, 2020

Model calibration data period: July 19, 2012, through September 24, 2019

Model application date: July 19, 2012, onward

Model-Calibration Dataset

All data were collected using USGS protocols (Wagner and others, 2006; U.S. Geological Survey, variously dated) and are stored in the National Water Information System (U.S. Geological Survey, 2020) database and available to the public. Ordinary least squares analysis was used to develop regression models using R programming language (R Core Team, 2020). Potential explanatory variables that were evaluated individually and in combination included streamflow, water temperature, SC, dissolved oxygen, pH, turbidity, chlorophyll and phycocyanin fluorescence, and UV nitrate sensor data. The maximum time span between two continuous data points used for interpolation was 2 hours (in order to preserve the sample dataset, field monitor averages obtained during sample collection were used for model development data if no continuous data were available or if gaps larger than 1 hour in the continuous data record resulted in missing interpolated data). Seasonal components (sine and cosine variables) were also evaluated as potential explanatory variables.

The final selected regression model was based on 132 concurrent measurements of Ca concentration and sensor-measured SC during July 19, 2012, through September 24, 2019. Samples were collected throughout the range of continuously observed hydrologic conditions. No samples had concentrations below laboratory detection limits. Summary statistics and the complete model-calibration dataset are provided below. Potential outliers were identified using the methods described in Rasmussen and others (2009). Additionally, studentized residuals from the final model were inspected for values greater than three or less than negative three. Values outside of that range were considered potential outliers and were investigated. One of the sensor-measured SC samples, from June 3, 2013, was deemed an outlier and removed from the model calibration dataset. The removed sensor-measured SC value was significantly lower than the field monitor and laboratory result during this sample. All other potential outliers were not found to have errors associated with collection, processing, or analysis and were therefore considered valid.

This model is specific to the Kansas River at De Soto, Kans., during this study period and cannot be applied to data collected from other sites on the Kansas River or data collected from other waterbodies.

Calcium Sampling Details

Cross-section samples typically were collected either from the downstream side of the bridge or instream within 100 feet of the bridge. The equal-width-increment collection method was used (although multiple vertical, single vertical, and grab samples were occasionally collected), and samples typically were composited for analysis (U.S. Geological Survey, variously dated). During July 2012 through June 2017, cross-section samples were collected every 2 weeks during March through October, once a month during

November through February, and during selected reservoir release and runoff events. During July 2017 through September 2019, cross-section samples were collected on a monthly to bimonthly basis, depending on flow conditions. A FISP US DH–81, DH–95, D–95, D–96a, or D–96 depth integrating sampler was used. Additional detail on sample collection is available in Foster and Graham (2016) and Graham and others (2018). Samples were analyzed for Ca concentration at the USGS National Water Quality Laboratory in Lakewood, Colorado.

Model Development

Ordinary least squares regression analysis was done using R programming language (R Core Team, 2020) to relate discretely collected Ca concentration to sensor-measured SC. The distribution of residuals was examined for normality, and the plots of residuals (the difference between the measured and computed values) were examined for homoscedasticity (departures from zero did not change substantially over the range of computed values). Previously published explanatory variables were also strongly considered for continuity.

SC was selected as a good surrogate for Ca based on residual plots, coefficient of determination (R^2), and model standard percentage error. Values for all the aforementioned statistics were computed and are included below along with all relevant sample data and additional statistical information.

Model Summary

The following is a summary of final regression analysis for Ca concentration at USGS site 06892350:

Ca concentration-based model:

$$\log Ca = 0.658 \times \log SC - 0.0415$$

where

\log = logarithm base 10;

Ca = calcium concentration, in milligrams per liter; and

SC = specific conductance, in microsiemens per centimeter at 25 degrees Celsius.

SC makes physical and statistical sense as an explanatory variable for Ca because of its positive correlation with charged ionic species (Hem, 1992).

The logarithmically (\log) transformed model may be retransformed to the original units so that Ca can be calculated directly. The retransformation introduces a bias in the calculated constituent. This bias may be corrected using Duan's bias correction factor (BCF; Duan, 1983). For this model, the calculated BCF is 1.01. The retransformed model, accounting for BCF is as follows:

$$Ca = 1.01 \times (SC^{0.658} \times 10^{-0.0415})$$

Previous Models

Start Year	End Year	Model Equation	Reference
2012	2019	$\log Ca = 0.645 \log SC - 0.03$	Foster and Graham (2016)
1999	2003	$\log Ca = 0.730 \log SC - 0.287$	Rasmussen and others (2005)

Model Statistics, Data, and Plots

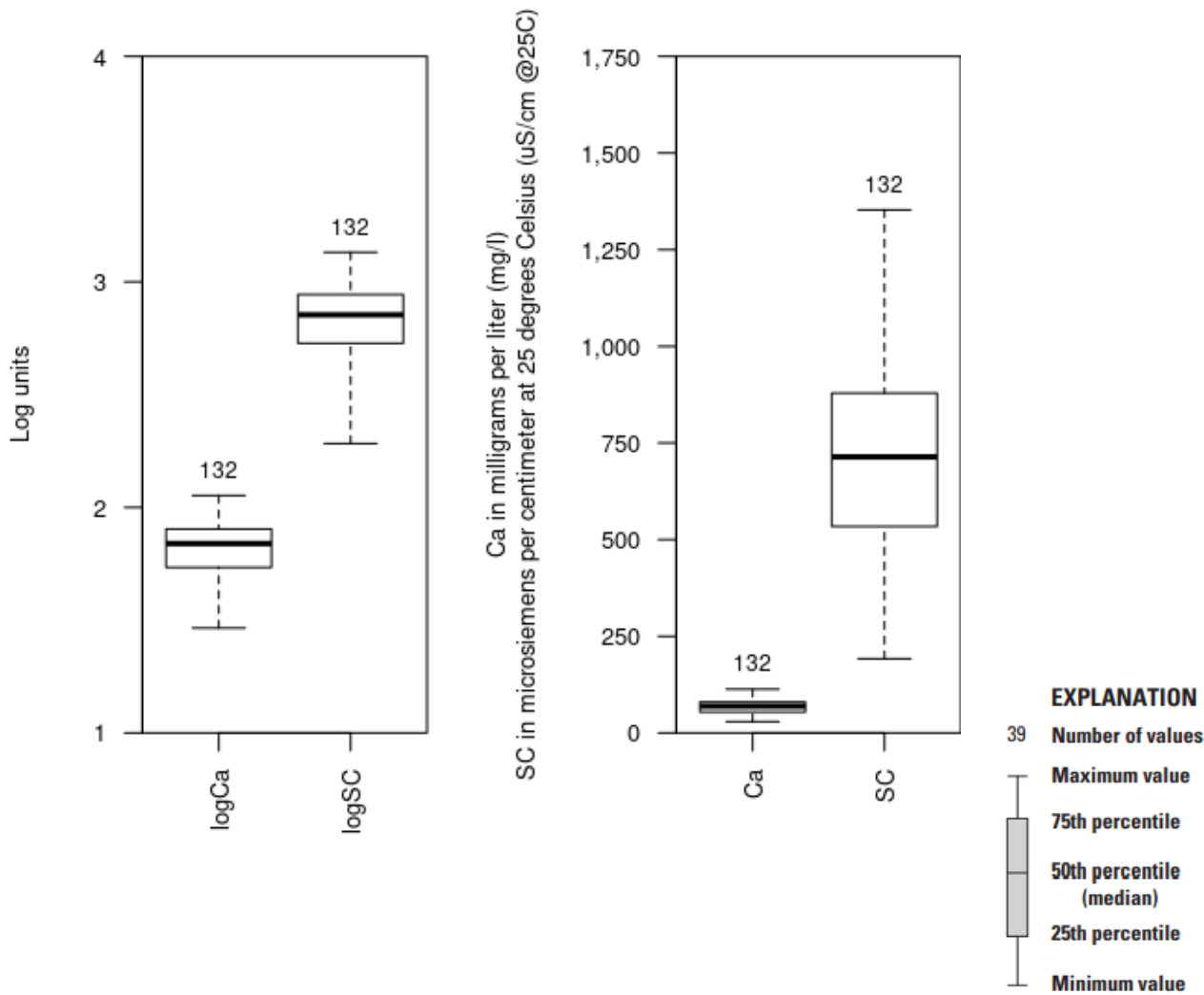
Model

$\text{logCa} = + 0.658 * \text{logSC} - 0.0415$

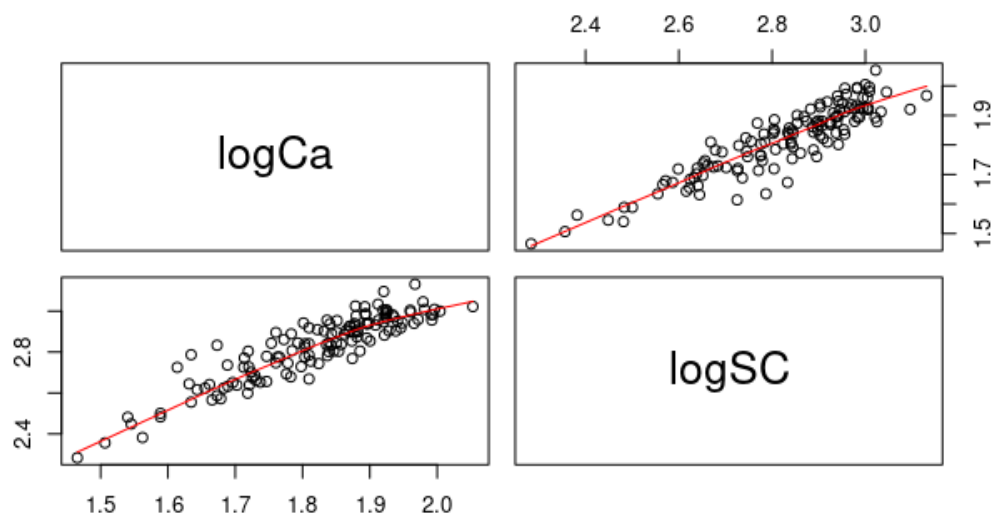
Variable Summary Statistics

	logCa	Ca	logSC	SC
Minimum	1.47	29.2	2.28	192
1st Quartile	1.73	54.2	2.73	534
Median	1.84	69.2	2.85	714
Mean	1.82	68.1	2.83	712
3rd Quartile	1.90	80.3	2.94	879
Maximum	2.05	113.0	3.13	1350

Box Plots



Exploratory Plots



Red line shows the locally weighted scatterplot smoothing (LOWESS).

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	132
Standard error (RMSE)	0.0497
Average Model standard percentage error (MSPE)	11.5
Coefficient of determination (R^2)	0.821
Adjusted Coefficient of Determination (Adj. R^2)	0.82
Bias Correction Factor (BCF)	1.01

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(> t)
(Intercept)	-0.0415	0.0763	-0.544	5.87e-01
logSC	0.6580	0.0270	24.400	2.13e-50

Correlation Matrix

	Intercept	E.vars
Intercept	1.000	-0.998
E.vars	-0.998	1.000

Outlier Test Criteria

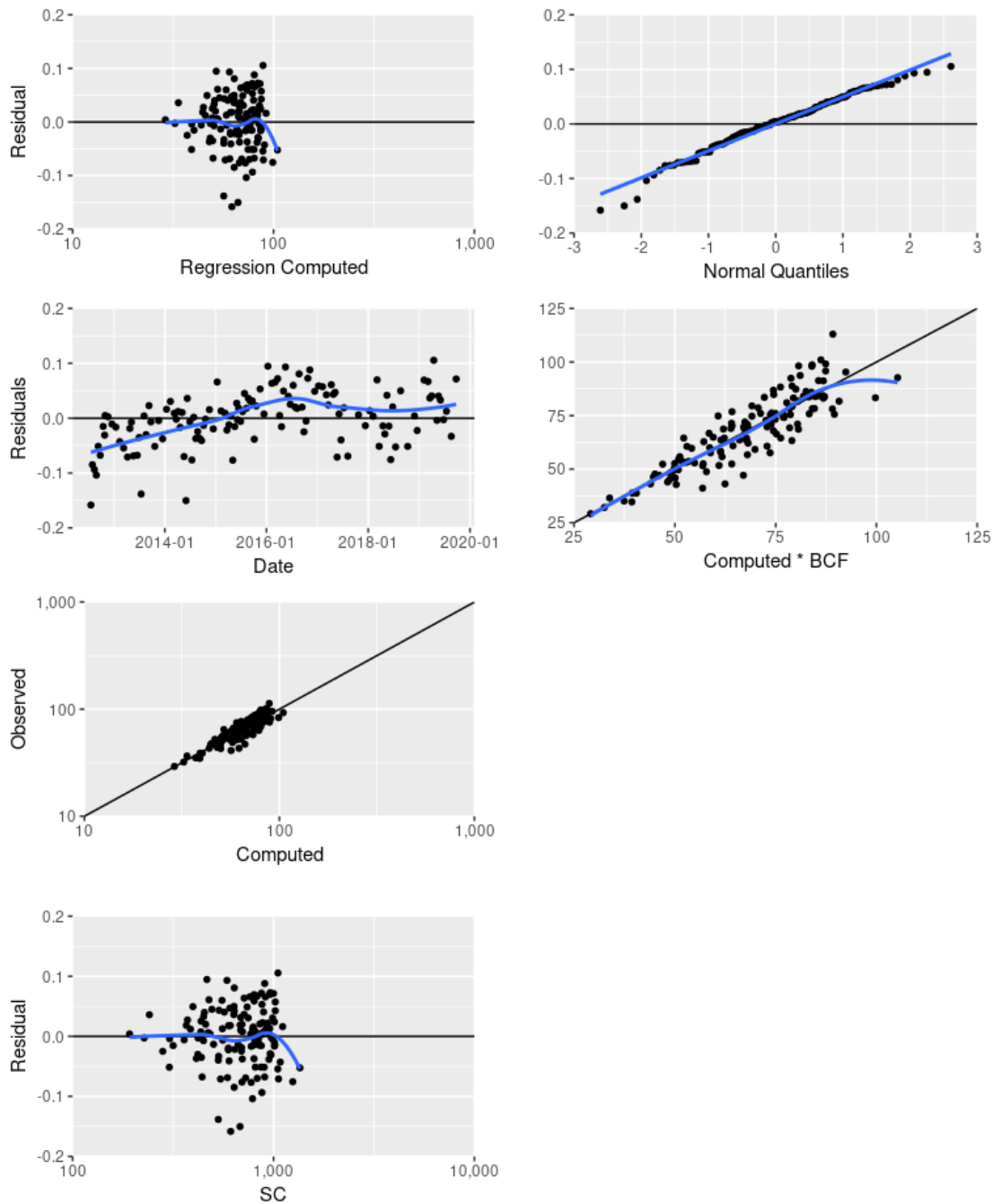
Leverage	Cook's D	DFFITS
0.0455	0.1945	0.2462

Flagged Observations

	logCa	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
201207190935	1.63	1.79	-0.15800	-3.2000	-3.3200	0.00802	0.041300	-0.2980
201307151040	1.61	1.75	-0.13800	-2.8000	-2.8700	0.01050	0.041700	-0.2970
201308051130	1.47	1.46	0.00402	0.0850	0.0847	0.09400	0.000375	0.0273
201406021300	1.67	1.82	-0.15000	-3.0300	-3.1300	0.00759	0.035200	-0.2740
201406111600	1.56	1.53	0.03600	0.7480	0.7470	0.06540	0.019600	0.1980
201506061950	1.51	1.51	-0.00272	-0.0568	-0.0566	0.07240	0.000126	-0.0158
201609261030	1.55	1.57	-0.02490	-0.5140	-0.5130	0.04930	0.006850	-0.1170

2018061111000	1.92	2.00	-0.07550	-1.5400	-1.5500	0.02900	0.035500	-0.2680
201904160930	2.05	1.95	0.10600	2.1400	2.1700	0.01890	0.044200	0.3020

Statistical Plots



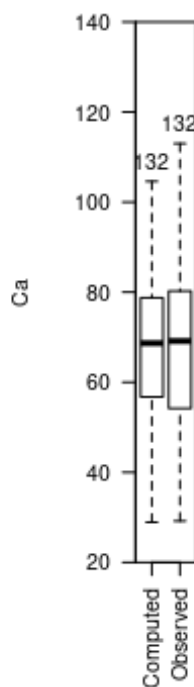
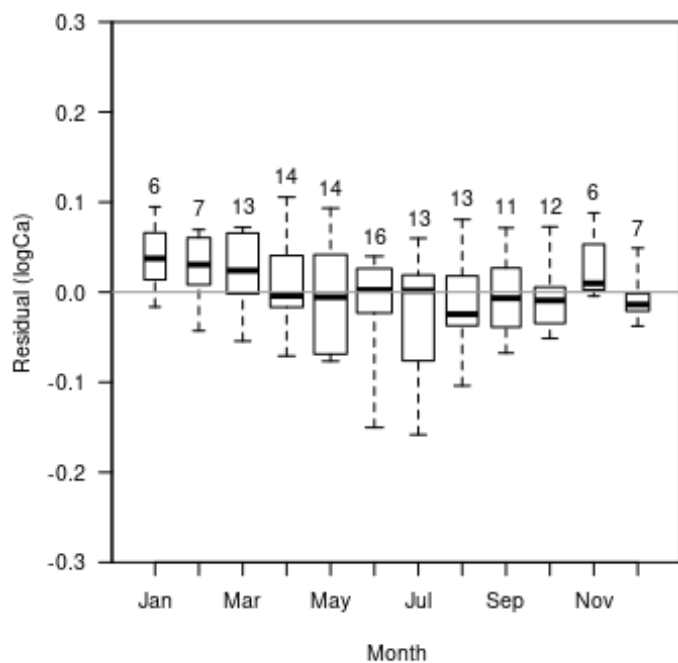
First row (left): Residual Ca related to regression computed Ca with local polynomial regression fitting, or locally estimated scatterplot smoothing (LOESS), indicated by the blue line.

First row (right): Residual Ca related to the corresponding normal quantile of the residual with simple linear regression, indicated by the blue line.

Second row: Residual Ca related to date (left) and regression computed Ca multiplied by the BCF (right) with LOESS, indicated by the blue line.

Third row: Observed Ca related to regression computed Ca.

Fourth row: Residual Ca related to SC with LOESS, indicated by the blue line.



EXPLANATION

39 Number of values

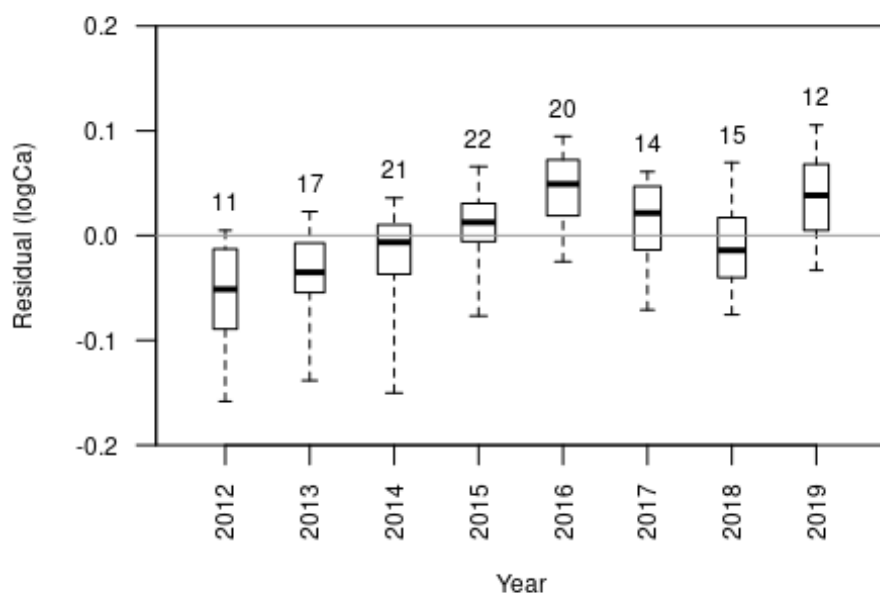
Maximum value

75th percentile

50th percentile (median)

25th percentile

Minimum value



EXPLANATION

39 Number of values

Maximum value

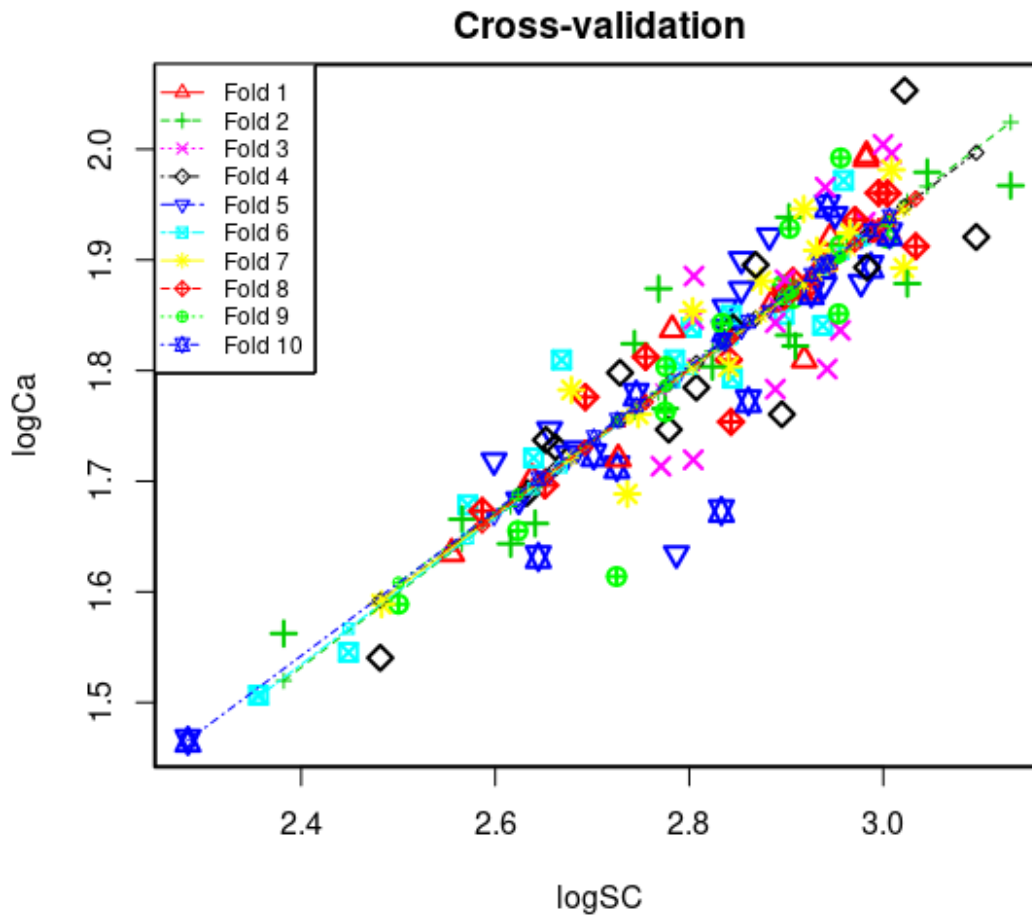
75th percentile

50th percentile (median)

25th percentile

Minimum value

Cross-Validation



Fold - equal partition of the data (10 percent of the data).

Large symbols - observed value of a data point removed in a fold.

Small symbols - recomputed value of a data point removed in a fold.

Recomputed regression lines - adjusted regression line with one fold removed.

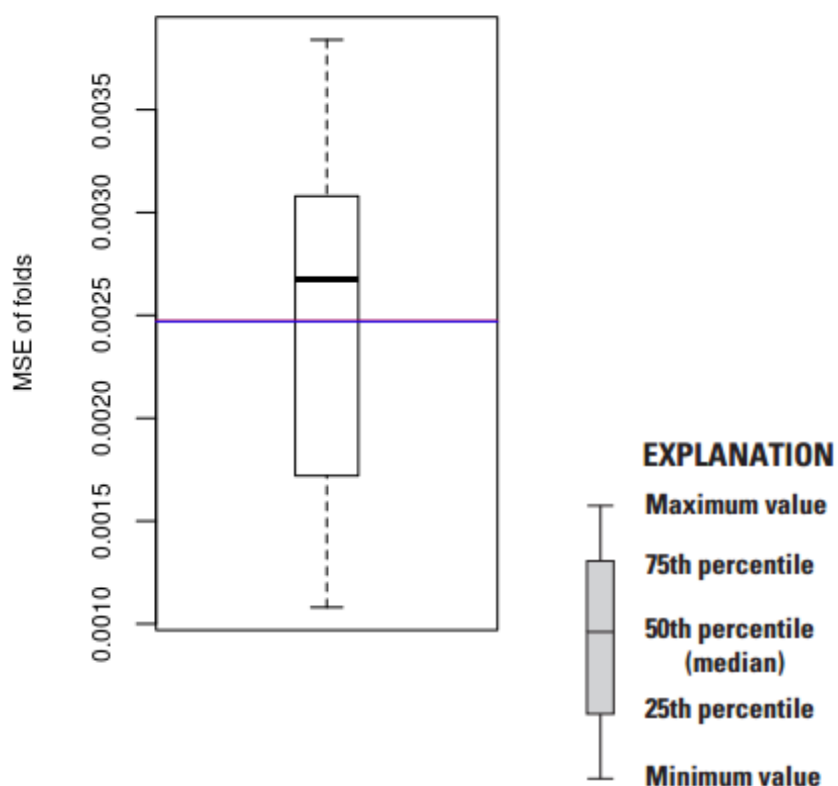
Minimum MSE of folds: 0.00108

Mean MSE of folds: 0.00247

Median MSE of folds: 0.00268

Maximum MSE of folds: 0.00384

(Mean MSE of folds) / (Model MSE): 0.99900



Red line - Model MSE

Blue line - Mean MSE of folds

Model-Calibration Dataset

	Date	logCa	logSC	Ca	SC	Computed logCa	Computed Ca	Residual	Normal Quantiles	Censored Values
0										
1	2012-07-19	1.63	2.79	43.1	612	1.79	62.4	-0.158	-2.61	--
2	2012-07-30	1.72	2.8	52.4	637	1.8	64.1	-0.0848	-1.72	--
3	2012-08-13	1.8	2.94	63.3	875	1.9	79	-0.0936	-1.81	--
4	2012-08-27	1.76	2.9	57.6	786	1.86	73.6	-0.104	-1.92	--
5	2012-09-10	1.84	2.94	69.3	866	1.89	78.5	-0.0512	-0.981	--
6	2012-09-24	1.84	2.96	68.6	903	1.9	80.7	-0.0676	-1.19	--
7	2012-10-15	1.85	2.9	70.9	790	1.87	73.9	-0.0151	-0.42	--
8	2012-10-26	1.89	2.99	78.3	971	1.92	84.6	-0.0309	-0.709	--
9	2012-10-29	1.92	2.98	83.7	948	1.92	83.3	0.0049	0.0664	--
10	2012-11-19	1.89	2.94	78.5	867	1.89	78.5	0.00258	-0.0474	--
11	2012-12-17	1.93	3	84.2	1010	1.94	86.8	-0.0106	-0.298	--
12	2013-01-14	1.92	3	83.1	1010	1.94	86.8	-0.0163	-0.483	--
13	2013-02-11	1.91	3.03	81.7	1080	1.96	90.7	-0.0429	-0.95	--
14	2013-03-11	1.89	3.02	78.1	1050	1.95	89.1	-0.0544	-1.15	--
15	2013-04-08	1.88	3.02	75.6	1060	1.95	89.6	-0.0708	-1.4	--
16	2013-04-25	1.81	2.84	64.5	693	1.83	67.8	-0.0187	-0.526	--
17	2013-05-06	1.7	2.65	49.7	448	1.7	50.9	-0.0072	-0.278	--
18	2013-05-20	1.71	2.77	51.7	590	1.78	61	-0.0688	-1.27	--
19	2013-06-17	1.63	2.64	42.8	441	1.7	50.3	-0.0676	-1.22	--
20	2013-07-01	1.66	2.64	45.9	438	1.7	50.1	-0.0351	-0.759	--

21	2013-07-15	1.61	2.73	41.1	531	1.75	56.9	-0.138	-2.06	--
22	2013-08-05	1.47	2.28	29.2	192	1.46	29.1	0.00402	0.00948	--
23	2013-08-19	1.66	2.62	45.2	420	1.69	48.7	-0.03	-0.685	--
24	2013-09-09	1.92	2.95	83.2	882	1.9	79.4	0.0229	0.504	--
25	2013-09-23	1.87	2.91	73.3	807	1.87	74.9	-0.00669	-0.259	--
26	2013-10-21	1.85	2.95	71	899	1.9	80.4	-0.0514	-1.04	--
27	2013-11-18	1.93	3	84.3	990	1.93	85.7	-0.00439	-0.181	--
28	2013-12-16	1.79	2.84	62.1	699	1.83	68.2	-0.0376	-0.837	--
29	2014-01-13	1.98	3.05	95.3	1110	1.96	92.4	0.0162	0.318	--
30	2014-02-10	1.96	3	91.3	989	1.93	85.6	0.0305	0.592	--
31	2014-03-10	1.88	2.91	76	807	1.87	74.9	0.00902	0.143	--
32	2014-03-24	1.92	2.99	83.9	974	1.93	84.8	-0.00189	-0.104	--
33	2014-04-07	1.88	2.9	75.3	787	1.86	73.7	0.0122	0.22	--
34	2014-04-21	1.84	2.89	69.7	774	1.86	72.9	-0.0166	-0.504	--
35	2014-05-05	1.84	2.84	68.5	686	1.83	67.3	0.0103	0.181	--
36	2014-05-19	1.81	2.92	64.5	829	1.88	76.2	-0.0699	-1.35	--
37	2014-06-02	1.67	2.83	47.1	681	1.82	67	-0.15	-2.25	--
38	2014-06-11	1.56	2.38	36.5	241	1.53	33.8	0.036	0.685	--
39	2014-06-30	1.76	2.75	57.6	559	1.77	58.8	-0.00641	-0.239	--
40	2014-07-14	1.75	2.84	56.7	697	1.83	68	-0.0762	-1.58	--
41	2014-07-28	1.87	2.9	73.9	793	1.87	74.1	0.00174	-0.0664	--
42	2014-08-11	1.83	2.9	67.9	799	1.87	74.4	-0.0372	-0.811	--
43	2014-08-25	1.8	2.84	63.6	692	1.83	67.7	-0.0245	-0.615	--
44	2014-09-08	1.64	2.62	44	413	1.68	48.2	-0.0369	-0.785	--
45	2014-09-22	1.75	2.78	55.8	601	1.79	61.7	-0.0409	-0.921	--
46	2014-10-06	1.72	2.7	52.9	503	1.74	54.9	-0.0132	-0.338	--
47	2014-10-20	1.69	2.63	48.9	429	1.69	49.4	-0.00186	-0.0854	--
48	2014-11-17	1.88	2.9	76.2	792	1.87	74	0.0155	0.298	--
49	2014-12-15	1.77	2.78	58.3	596	1.79	61.4	-0.0195	-0.548	--
50	2015-01-12	1.92	2.88	83.5	763	1.86	72.2	0.0659	1.35	--
51	2015-02-09	1.93	2.98	85.9	958	1.92	83.9	0.0132	0.259	--
52	2015-03-09	1.91	2.96	81.8	902	1.9	80.6	0.00915	0.162	--
53	2015-03-23	1.78	2.81	60.9	642	1.81	64.4	-0.0217	-0.57	--
54	2015-04-06	1.87	2.92	74.3	840	1.88	76.9	-0.0121	-0.318	--
55	2015-04-20	1.86	2.89	72.8	770	1.86	72.6	0.00388	-0.00948	--
56	2015-05-04	1.78	2.89	60.7	774	1.86	72.9	-0.0767	-1.65	--
57	2015-05-18	1.59	2.5	38.8	316	1.6	40.5	-0.0154	-0.44	--
58	2015-06-01	1.68	2.57	47.7	373	1.65	45.1	0.0273	0.57	--
59	2015-06-06	1.51	2.36	32.1	227	1.51	32.5	-0.00272	-0.124	--
60	2015-06-15	1.67	2.57	46.3	368	1.65	44.7	0.0183	0.379	--
61	2015-06-29	1.63	2.56	43.1	359	1.64	44	-0.00577	-0.22	--
62	2015-07-13	1.67	2.59	47.1	386	1.66	46.1	0.012	0.2	--
63	2015-07-27	1.78	2.69	59.7	493	1.73	54.2	0.0451	0.921	--
64	2015-08-10	1.81	2.78	64.5	609	1.79	62.3	0.0181	0.358	--
65	2015-08-24	1.84	2.8	69	634	1.8	63.9	0.036	0.709	--
66	2015-09-08	1.88	2.87	76	748	1.85	71.3	0.0307	0.615	--
67	2015-09-21	1.86	2.84	72	687	1.83	67.4	0.0316	0.638	--
68	2015-10-05	1.88	2.98	75.8	949	1.92	83.3	-0.0384	-0.865	--
69	2015-10-19	1.94	2.97	86.3	935	1.91	82.5	0.0221	0.483	--
70	2015-11-16	1.95	2.94	88.8	876	1.9	79.1	0.0532	1.08	--
71	2015-12-14	1.7	2.64	50.4	435	1.69	49.9	0.00751	0.104	--
72	2016-01-11	1.81	2.67	64.5	466	1.71	52.2	0.0947	2.25	--
73	2016-02-08	1.9	2.85	79.5	714	1.84	69.1	0.0636	1.27	--
74	2016-03-03	1.97	2.96	93.7	910	1.91	81.1	0.0656	1.31	--
75	2016-03-21	1.97	2.94	92.4	871	1.89	78.8	0.072	1.65	--

76	2016-04-04	1.9	2.94	78.8	865	1.89	78.4	0.0049	0.0474	--
77	2016-04-18	1.88	2.94	75.4	869	1.89	78.6	-0.0156	-0.461	--
78	2016-05-02	1.72	2.6	52.3	397	1.67	47	0.0495	1.01	--
79	2016-05-16	1.87	2.77	74.8	587	1.78	60.7	0.0933	2.06	--
80	2016-06-06	1.75	2.66	55.8	453	1.71	51.2	0.0399	0.759	--
81	2016-06-20	1.72	2.64	52.6	436	1.7	50	0.0252	0.548	--
82	2016-07-11	1.82	2.74	66.7	554	1.76	58.5	0.0599	1.19	--
83	2016-07-25	1.85	2.84	70.8	697	1.83	68	0.0201	0.44	--
84	2016-08-08	1.8	2.78	63.6	597	1.79	61.4	0.0178	0.338	--
85	2016-08-22	1.89	2.8	76.8	638	1.8	64.2	0.0807	1.81	--
86	2016-09-12	1.73	2.66	53.8	459	1.71	51.7	0.0201	0.42	--
87	2016-09-26	1.55	2.45	35.1	281	1.57	37.4	-0.0249	-0.638	--
88	2016-10-11	1.88	2.92	75.5	840	1.88	76.9	-0.0053	-0.2	--
89	2016-10-24	1.99	2.98	98.7	961	1.92	84	0.0726	1.72	--
90	2016-11-07	1.99	2.96	98.2	904	1.9	80.7	0.088	1.92	--
91	2016-12-12	1.9	2.87	78.6	739	1.85	70.7	0.0489	0.981	--
92	2017-01-09	1.93	2.9	84.8	801	1.87	74.5	0.0589	1.15	--
93	2017-02-06	2	3.01	99.1	1020	1.94	87.4	0.0573	1.11	--
94	2017-03-06	1.98	3.01	95.8	1020	1.94	87.4	0.0426	0.865	--
95	2017-03-20	1.96	3	91.2	1010	1.94	86.8	0.0241	0.526	--
96	2017-04-10	1.78	2.68	60.6	477	1.72	53	0.061	1.22	--
97	2017-04-25	1.8	2.73	62.8	535	1.75	57.2	0.0435	0.892	--
98	2017-05-08	1.84	2.78	68.7	606	1.79	62	0.047	0.95	--
99	2017-05-22	1.69	2.74	48.8	545	1.76	57.8	-0.071	-1.46	--
100	2017-06-05	1.84	2.85	69	700	1.83	68.2	0.00772	0.124	--
101	2017-06-19	1.71	2.73	51.6	531	1.75	56.9	-0.0397	-0.892	--
102	2017-07-10	1.84	2.83	69.6	682	1.82	67	0.019	0.399	--
103	2017-08-07	1.77	2.86	59.2	726	1.84	69.9	-0.0692	-1.31	--
104	2017-10-23	1.73	2.67	53.1	473	1.72	52.7	0.0062	0.0854	--
105	2017-12-11	1.8	2.82	63.6	667	1.82	66.1	-0.0137	-0.358	--
106	2018-01-10	1.92	2.97	84	924	1.91	81.9	0.0138	0.278	--
107	2018-02-05	1.9	2.94	79.2	876	1.9	79.1	0.00348	-0.0284	--
108	2018-03-05	1.99	2.98	98	960	1.92	84	0.0698	1.51	--
109	2018-03-20	1.82	2.91	66.4	812	1.87	75.2	-0.0513	-1.01	--
110	2018-04-16	1.92	3.01	83.8	1010	1.94	87.1	-0.0141	-0.379	--
111	2018-04-30	1.89	2.98	78.2	962	1.92	84.1	-0.0288	-0.661	--
112	2018-05-15	1.85	2.8	70.2	638	1.8	64.2	0.0417	0.837	--
113	2018-05-29	1.87	2.93	74.1	843	1.88	77.1	-0.0144	-0.399	--
114	2018-06-11	1.92	3.1	83.3	1250	2	99.7	-0.0755	-1.51	--
115	2018-06-25	1.91	2.93	81	854	1.89	77.8	0.0205	0.461	--
116	2018-07-16	1.97	3.13	92.7	1350	2.02	105	-0.0524	-1.11	--
117	2018-08-21	1.85	2.8	71.4	636	1.8	64	0.0499	1.04	--
118	2018-10-11	1.54	2.48	34.7	303	1.59	39.3	-0.0514	-1.08	--
119	2018-11-29	1.73	2.68	53.6	483	1.73	53.4	0.0041	0.0284	--
120	2018-12-18	1.76	2.78	57.9	596	1.79	61.4	-0.0225	-0.592	--
121	2019-02-06	1.94	2.9	86.8	799	1.87	74.4	0.0695	1.46	--
122	2019-03-06	1.95	2.92	88.3	828	1.88	76.2	0.0668	1.4	--
123	2019-03-19	1.87	2.85	74.7	714	1.84	69.1	0.0365	0.734	--
124	2019-04-01	1.94	2.95	87.3	892	1.9	80	0.0406	0.811	--
125	2019-04-16	2.05	3.02	113	1050	1.95	89.2	0.106	2.61	--
126	2019-05-09	1.59	2.48	38.8	304	1.59	39.4	-0.00388	-0.162	--
127	2019-05-20	1.81	2.76	64.9	569	1.77	59.5	0.0403	0.785	--
128	2019-06-03	1.74	2.65	54.6	449	1.7	50.9	0.033	0.661	--
129	2019-06-26	1.68	2.62	48.2	421	1.69	48.8	-0.00274	-0.143	--
130	2019-07-16	1.78	2.75	60	556	1.77	58.6	0.0127	0.239	--

131	2019-08-20	1.72	2.73	52.5	533	1.75	57	-0.0331	-0.734	--
132	2019-09-24	2	3	101	999	1.93	86.2	0.0714	1.58	--

Definitions

Ca: Calcium, in milligrams per liter (00915).

Cook's D: Cook's distance (Helsel and others, 2020).

DIFFITS: Difference in fits statistic (Helsel and others, 2020).

E.vars: Explanatory variables.

Leverage: An outlier's measure 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).

MSE: Model standard error (Helsel and others, 2020).

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

Probability(>|t|): The 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).

SC: Specific conductance, in microsiemens per centimeter at 25 degrees Celsius (00095).

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

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