Appendix 14. Model Archival Summary for Hardness 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 hardness as calcium carbonate (CaCO$_3$; U.S. Geological Survey [USGS] parameter code 00900) concentration model developed to compute 15-minute CaCO$_3$ concentrations from July 2012 onward. This model supersedes all previous models.

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

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 26, 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 CaCO$_3$ 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.

Hardness 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 $CaCO_3$ 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 $CaCO_3$ 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 $CaCO_3$ 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 $CaCO_3$ concentration at USGS site 06892350:

$CaCO_3$ concentration-based model:

$$\log CaCO_3 = 0.712 \times \log SC + 0.343$$

where

$\log$ = logarithm base 10;

$CaCO_3$ = hardness as calcium carbonate 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 $CaCO_3$ 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 $CaCO_3$ 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 1.00. The retransformed model, accounting for BCF is as follows:

$$CaCO_3 = 1 \times (SC^{0.712} \times 10^{0.343})$$

Previous Models

There are no previously published models for hardness as calcium carbonate at this site.
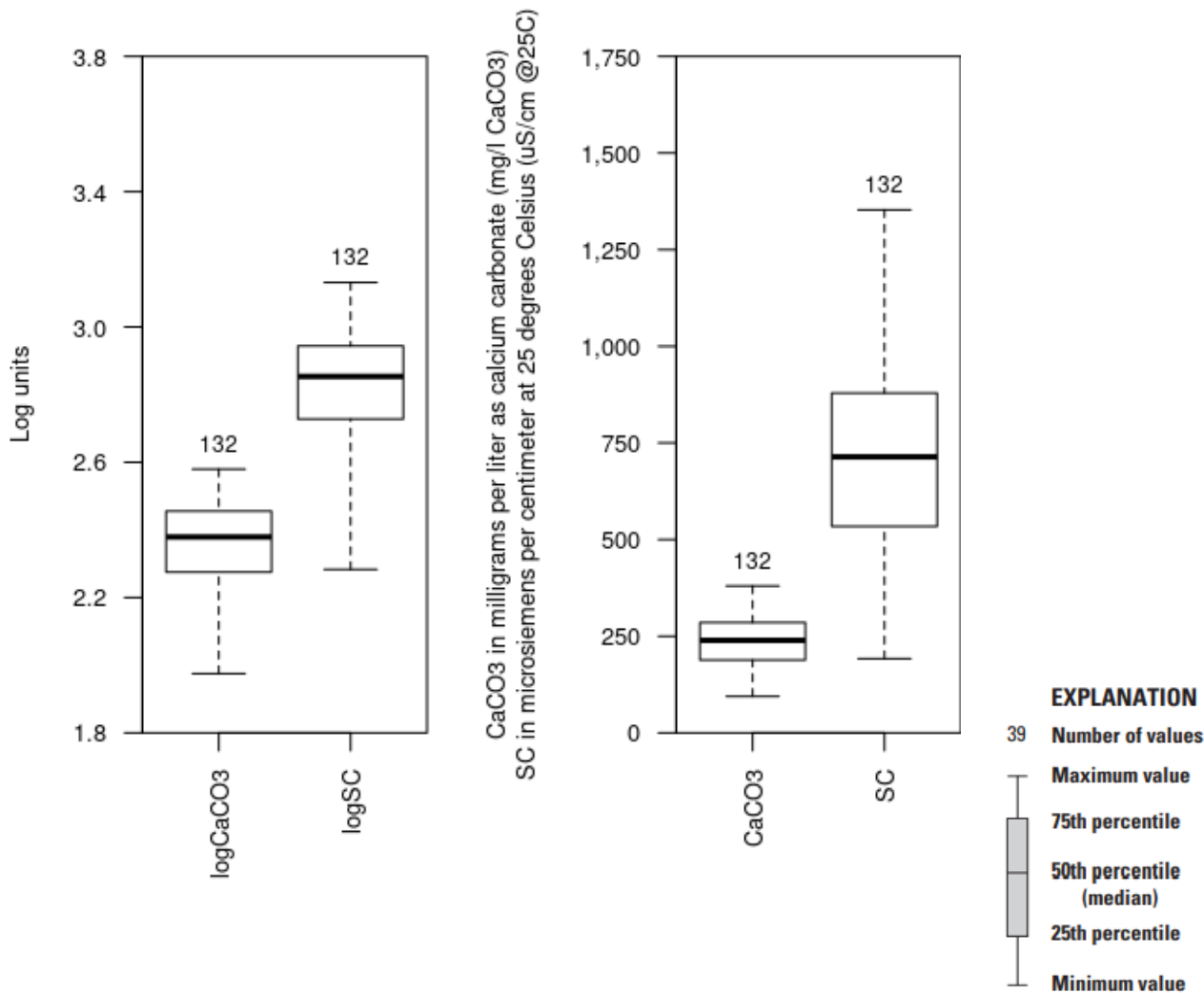
Model Statistics, Data, and Plots
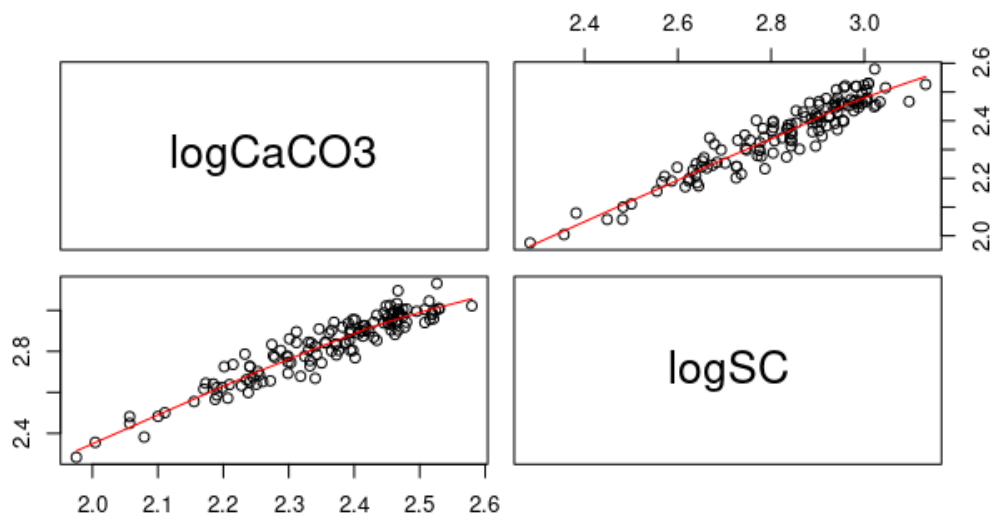
Model

logCaCO3 = + 0.712 * logSC + 0.343

Variable Summary Statistics

```
              logCaCO3 CaCO3 logSC    SC
Minimum           1.98  94.5  2.28   192
1st Quartile      2.28 188.0  2.73   534
Median            2.38 240.0  2.85   714
Mean              2.36 235.0  2.83   712
3rd Quartile      2.46 285.0  2.94   879
Maximum           2.58 380.0  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)                           0.0409
Average Model standard percentage error (MSPE)    9.43
Coefficient of determination (R²)                0.888
Adjusted Coefficient of Determination (Adj. R²)  0.887
Bias Correction Factor (BCF)                         1
```

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(>|t|)
(Intercept)	0.343	0.0628	5.47	2.26e-07
logSC	0.712	0.0222	32.10	1.11e-63

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

|	logCaCO3	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
201308051130	1.98	1.97	0.00611	0.157	0.156	0.0940	0.00128	0.0504
201406111600	2.08	2.04	0.03960	1.000	1.000	0.0654	0.03500	0.2650
201506061950	2.00	2.02	-0.01680	-0.426	-0.425	0.0724	0.00709	-0.1190
201601111010	2.34	2.24	0.09680	2.390	2.430	0.0148	0.04290	0.2980
201609261030	2.06	2.09	-0.03020	-0.758	-0.757	0.0493	0.01490	-0.1720
201806111000	2.47	2.55	-0.08120	-2.010	-2.040	0.0290	0.06060	-0.3520
201810111350	2.06	2.11	-0.05350	-1.340	-1.340	0.0424	0.03960	-0.2820
201904160930	2.58	2.50	0.08430	2.080	2.110	0.0189	0.04170	0.2930

Statistical Plots
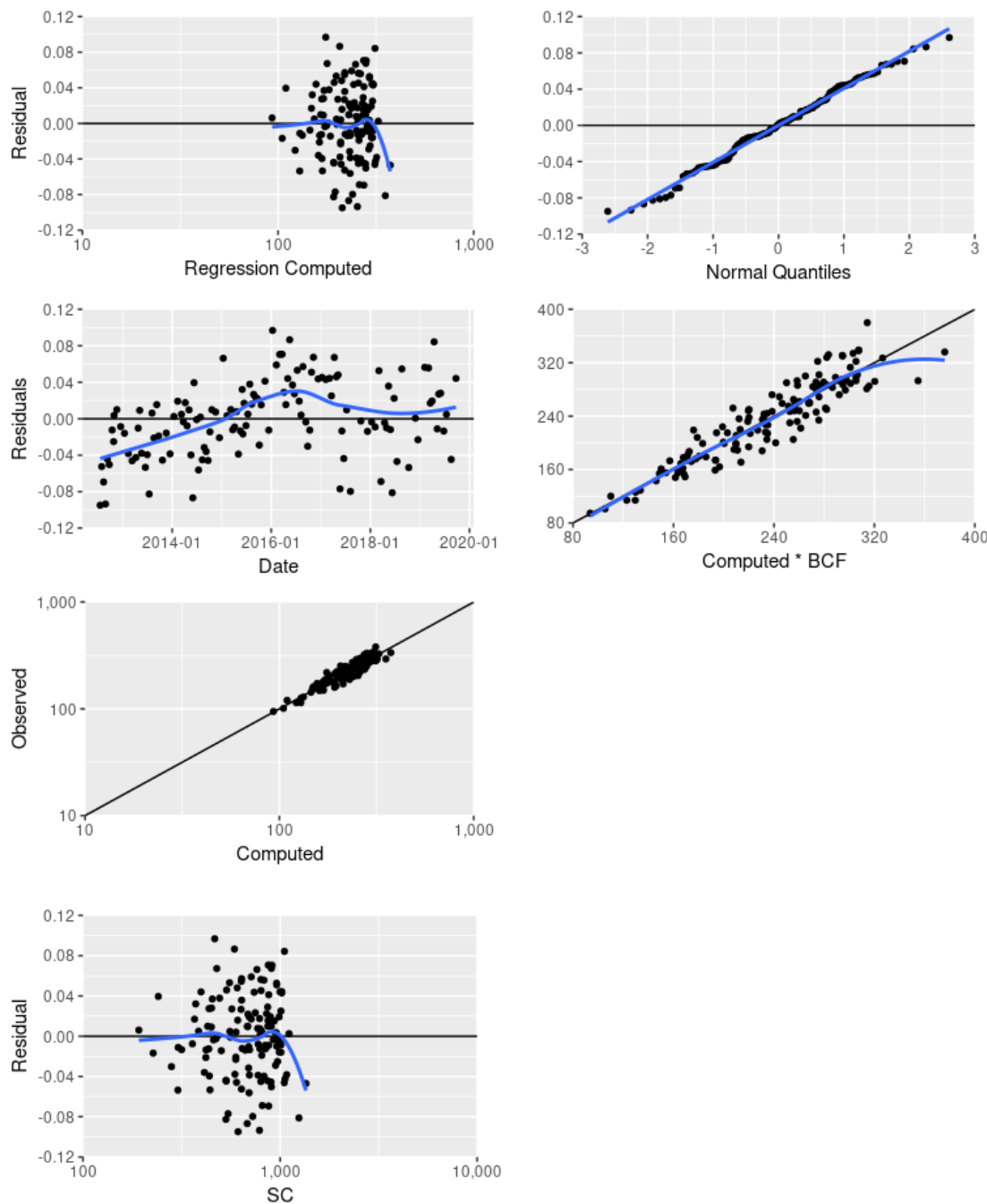
First row (left): Residual CaCO3 related to regression computed CaCO3 with local polynomial regression fitting, or locally estimated scatterplot smoothing (LOESS), indicated by the blue line.

First row (right): Residual CaCO3 related to the corresponding normal quantile of the residual with simple linear regression, indicated by the blue line.

Second row: Residual CaCO3 related to date (left) and regression computed CaCO3 multiplied by the BCF (right) with LOESS, indicated by the blue line.

Third row: Observed CaCO3 related to regression computed CaCO3.

Fourth row: Residual CaCO3 related to SC with LOESS, indicated by the blue line.
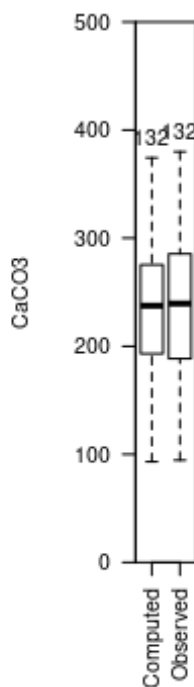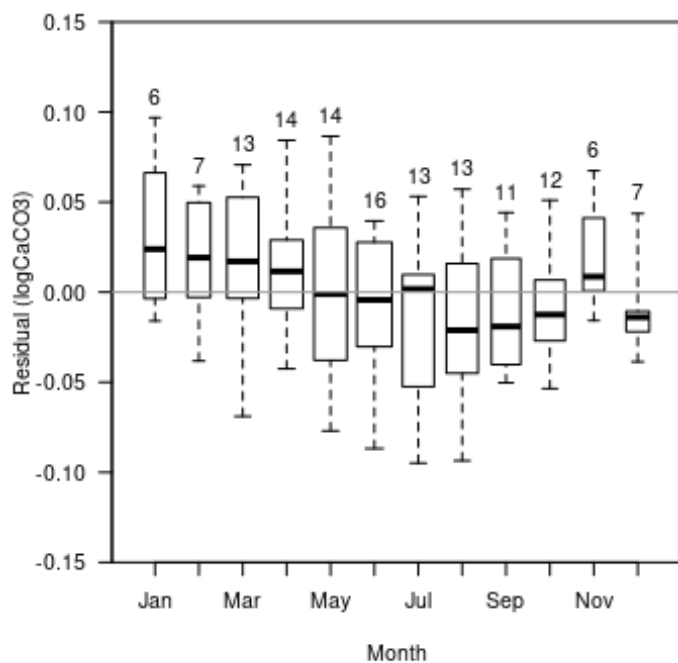
EXPLANATION

39   Number of values
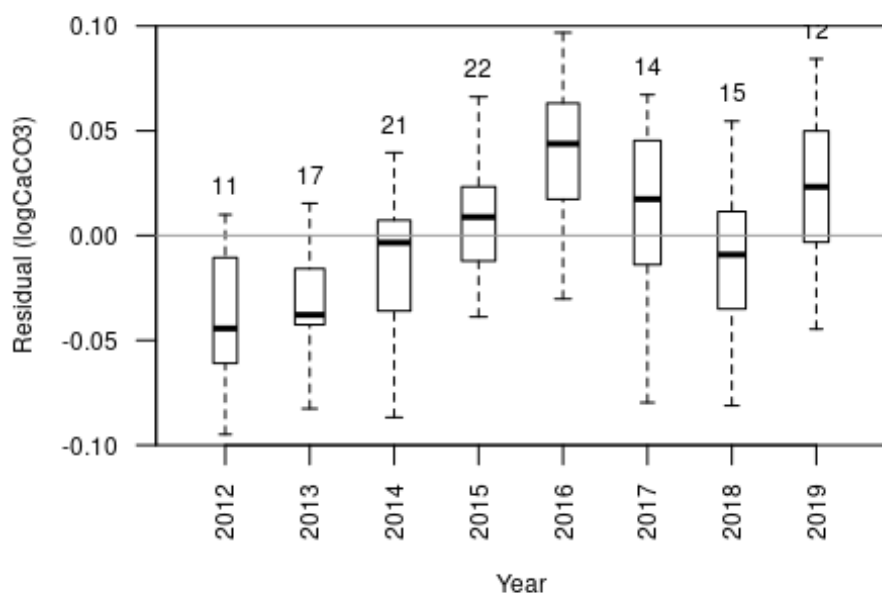
    Maximum value

    75th percentile

    50th percentile
    (median)

    25th percentile

    Minimum value
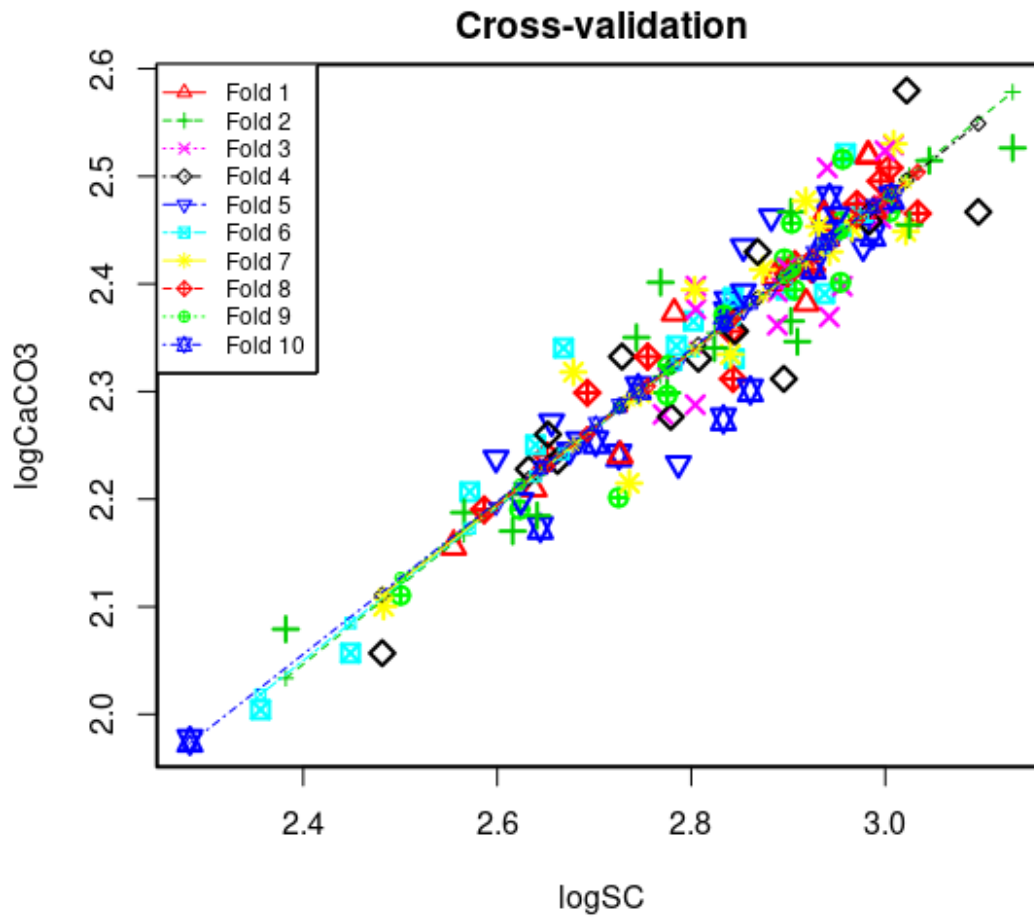

EXPLANATION

39   Number of values

    Maximum value

    75th percentile

    50th percentile
    (median)

    25th percentile

    Minimum value

Cross-Validation

Cross-validation plot of logCaCO3 versus logSC

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.
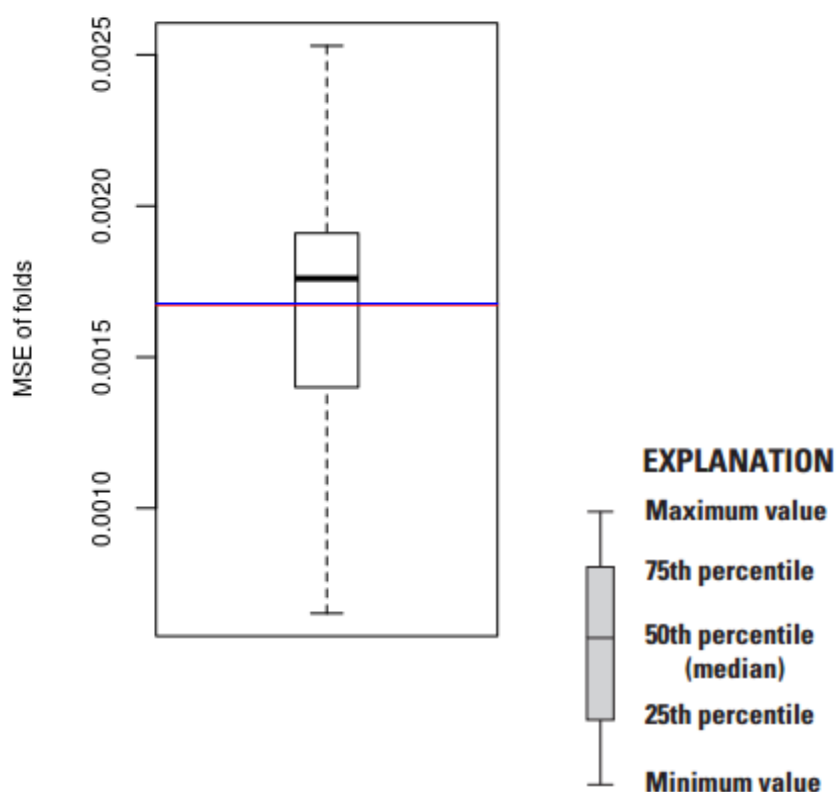
```
        Minimum MSE of folds:  0.000652
           Mean MSE of folds:  0.001680
         Median MSE of folds:  0.001760
        Maximum MSE of folds:  0.002530
(Mean MSE of folds) / (Model MSE):  1.000000
```

EXPLANATION

Maximum value

75th percentile

50th percentile
(median)

25th percentile

Minimum value

Red line - Model MSE

Blue line - Mean MSE of folds

Model-Calibration Dataset

	Date	logCaCO3	logSC	CaCO3	SC	Computed logCaCO3	Computed CaCO3	Residual	Normal Quantiles	Censored Values
0										
1	2012-07-19	2.23	2.79	171	612	2.33	214	-0.0949	-2.61	--
2	2012-07-30	2.29	2.8	194	637	2.34	220	-0.0525	-1.31	--
3	2012-08-13	2.37	2.94	234	875	2.44	276	-0.0694	-1.58	--
4	2012-08-27	2.31	2.9	205	786	2.41	255	-0.0935	-2.25	--
5	2012-09-10	2.39	2.94	246	866	2.44	274	-0.0443	-1.01	--
6	2012-09-24	2.4	2.96	250	903	2.45	282	-0.0503	-1.27	--
7	2012-10-15	2.39	2.9	248	790	2.41	256	-0.0124	-0.338	--
8	2012-10-26	2.45	2.99	279	971	2.47	297	-0.0251	-0.661	--
9	2012-10-29	2.47	2.98	293	948	2.46	292	0.0036	0.0664	--
10	2012-11-19	2.45	2.94	279	867	2.44	274	0.00996	0.298	--
11	2012-12-17	2.47	3	298	1010	2.48	305	-0.00865	-0.181	--
12	2013-01-14	2.47	3	293	1010	2.48	305	-0.016	-0.526	--
13	2013-02-11	2.47	3.03	292	1080	2.5	320	-0.0382	-0.811	--
14	2013-03-11	2.45	3.02	281	1050	2.49	314	-0.0462	-1.19	--
15	2013-04-08	2.45	3.02	285	1060	2.5	316	-0.0426	-0.95	--
16	2013-04-25	2.36	2.84	227	693	2.37	233	-0.0103	-0.259	--
17	2013-05-06	2.24	2.65	174	448	2.23	171	0.00914	0.22	--
18	2013-05-20	2.28	2.77	190	590	2.32	208	-0.0378	-0.785	--
19	2013-06-17	2.17	2.64	149	441	2.23	169	-0.0534	-1.35	--
20	2013-07-01	2.18	2.64	153	438	2.22	168	-0.0395	-0.892	--

21	2013-07-15	2.2	2.73	159	531	2.28	193	-0.0826	-1.92	--
22	2013-08-05	1.98	2.28	94.5	192	1.97	93.6	0.00611	0.162	--
23	2013-08-19	2.19	2.62	155	420	2.21	163	-0.0211	-0.615	--
24	2013-09-09	2.46	2.95	286	882	2.44	277	0.0154	0.358	--
25	2013-09-23	2.39	2.91	248	807	2.41	260	-0.019	-0.57	--
26	2013-10-21	2.4	2.95	252	899	2.45	281	-0.0454	-1.11	--
27	2013-11-18	2.46	3	289	990	2.48	301	-0.0158	-0.504	--
28	2013-12-16	2.33	2.84	214	699	2.37	235	-0.0386	-0.837	--
29	2014-01-13	2.51	3.05	327	1110	2.51	327	0.00248	0.0284	--
30	2014-02-10	2.5	3	313	989	2.48	301	0.0192	0.483	--
31	2014-03-10	2.42	2.91	262	807	2.41	260	0.00485	0.124	--
32	2014-03-24	2.47	2.99	294	974	2.47	298	-0.00339	-0.0664	--
33	2014-04-07	2.42	2.9	265	787	2.41	256	0.0176	0.461	--
34	2014-04-21	2.39	2.89	247	774	2.4	253	-0.00784	-0.162	--
35	2014-05-05	2.37	2.84	236	686	2.36	232	0.0097	0.239	--
36	2014-05-19	2.38	2.92	241	829	2.42	265	-0.0398	-0.921	--
37	2014-06-02	2.27	2.83	188	681	2.36	231	-0.0868	-2.06	--
38	2014-06-11	2.08	2.38	120	241	2.04	110	0.0396	0.865	--
39	2014-06-30	2.3	2.75	199	559	2.3	200	-0.00103	-0.0284	--
40	2014-07-14	2.31	2.84	205	697	2.37	234	-0.0562	-1.46	--
41	2014-07-28	2.41	2.9	257	793	2.41	257	0.00176	0.00948	--
42	2014-08-11	2.37	2.9	232	799	2.41	258	-0.045	-1.08	--
43	2014-08-25	2.33	2.84	216	692	2.37	233	-0.0316	-0.734	--
44	2014-09-08	2.17	2.62	148	413	2.21	161	-0.036	-0.759	--
45	2014-09-22	2.28	2.78	189	601	2.32	211	-0.0458	-1.15	--
46	2014-10-06	2.25	2.7	179	503	2.27	186	-0.0144	-0.483	--
47	2014-10-20	2.23	2.63	169	429	2.22	166	0.00988	0.278	--
48	2014-11-17	2.41	2.9	260	792	2.41	257	0.00732	0.181	--
49	2014-12-15	2.3	2.78	199	596	2.32	210	-0.0209	-0.592	--
50	2015-01-12	2.46	2.88	290	763	2.4	250	0.0663	1.58	--
51	2015-02-09	2.47	2.98	295	958	2.47	294	0.00331	0.0474	--
52	2015-03-09	2.46	2.96	287	902	2.45	282	0.01	0.318	--
53	2015-03-23	2.33	2.81	214	642	2.34	221	-0.0121	-0.318	--
54	2015-04-06	2.42	2.92	261	840	2.43	268	-0.00909	-0.22	--
55	2015-04-20	2.41	2.89	255	770	2.4	252	0.00774	0.2	--
56	2015-05-04	2.36	2.89	230	774	2.4	253	-0.0388	-0.865	--
57	2015-05-18	2.11	2.5	129	316	2.12	134	-0.0133	-0.399	--
58	2015-06-01	2.21	2.57	161	373	2.17	150	0.0321	0.759	--
59	2015-06-06	2	2.36	101	227	2.02	105	-0.0168	-0.548	--
60	2015-06-15	2.19	2.57	154	368	2.17	149	0.017	0.42	--
61	2015-06-29	2.16	2.56	143	359	2.16	146	-0.00757	-0.143	--
62	2015-07-13	2.19	2.59	155	386	2.19	154	0.005	0.143	--
63	2015-07-27	2.3	2.69	199	493	2.26	183	0.0378	0.837	--
64	2015-08-10	2.34	2.78	220	609	2.33	213	0.0159	0.399	--
65	2015-08-24	2.37	2.8	232	634	2.34	219	0.0267	0.638	--
66	2015-09-08	2.41	2.87	259	748	2.39	247	0.0233	0.592	--
67	2015-09-21	2.39	2.84	243	687	2.36	232	0.0219	0.548	--
68	2015-10-05	2.43	2.98	272	949	2.46	292	-0.0289	-0.685	--
69	2015-10-19	2.47	2.97	298	935	2.46	289	0.0152	0.338	--
70	2015-11-16	2.48	2.94	302	876	2.44	276	0.0412	0.892	--
71	2015-12-14	2.21	2.64	162	435	2.22	167	-0.0125	-0.358	--
72	2016-01-11	2.34	2.67	219	466	2.24	176	0.0968	2.61	--
73	2016-02-08	2.43	2.85	272	714	2.38	238	0.059	1.51	--
74	2016-03-03	2.52	2.96	332	910	2.45	283	0.0705	1.81	--
75	2016-03-21	2.51	2.94	322	871	2.44	275	0.0707	1.92	--

76	2016-04-04	2.46	2.94	291	865	2.43	273	0.029	0.734	--
77	2016-04-18	2.45	2.94	283	869	2.44	274	0.0154	0.379	--
78	2016-05-02	2.24	2.6	173	397	2.19	157	0.044	0.981	--
79	2016-05-16	2.4	2.77	252	587	2.31	207	0.0866	2.25	--
80	2016-06-06	2.27	2.66	187	453	2.23	172	0.037	0.811	--
81	2016-06-20	2.25	2.64	178	436	2.22	168	0.0274	0.685	--
82	2016-07-11	2.35	2.74	224	554	2.3	199	0.0531	1.27	--
83	2016-07-25	2.39	2.84	244	697	2.37	234	0.0193	0.504	--
84	2016-08-08	2.32	2.78	211	597	2.32	210	0.00406	0.0854	--
85	2016-08-22	2.4	2.8	250	638	2.34	220	0.0572	1.46	--
86	2016-09-12	2.24	2.66	172	459	2.24	174	-0.00361	-0.104	--
87	2016-09-26	2.06	2.45	114	281	2.09	123	-0.0302	-0.709	--
88	2016-10-11	2.41	2.92	259	840	2.43	268	-0.0126	-0.379	--
89	2016-10-24	2.52	2.98	330	961	2.47	295	0.051	1.19	--
90	2016-11-07	2.52	2.96	328	904	2.45	282	0.0674	1.72	--
91	2016-12-12	2.43	2.87	269	739	2.39	244	0.0437	0.95	--
92	2017-01-09	2.46	2.9	286	801	2.41	259	0.0453	1.08	--
93	2017-02-06	2.53	3.01	338	1020	2.49	307	0.043	0.921	--
94	2017-03-06	2.53	3.01	339	1020	2.49	307	0.0443	1.04	--
95	2017-03-20	2.51	3	322	1010	2.48	305	0.025	0.615	--
96	2017-04-10	2.32	2.68	208	477	2.25	179	0.0673	1.65	--
97	2017-04-25	2.33	2.73	215	535	2.29	194	0.0459	1.11	--
98	2017-05-08	2.37	2.78	236	606	2.32	212	0.0481	1.15	--
99	2017-05-22	2.21	2.74	164	545	2.29	197	-0.077	-1.65	--
100	2017-06-05	2.36	2.85	227	700	2.37	235	-0.0134	-0.42	--
101	2017-06-19	2.24	2.73	174	531	2.28	193	-0.0437	-0.981	--
102	2017-07-10	2.37	2.83	235	682	2.36	231	0.00975	0.259	--
103	2017-08-07	2.3	2.86	200	726	2.38	241	-0.0797	-1.72	--
104	2017-10-23	2.25	2.67	176	473	2.25	178	-0.00249	-0.0474	--
105	2017-12-11	2.34	2.82	219	667	2.35	227	-0.0139	-0.461	--
106	2018-01-10	2.45	2.97	283	924	2.46	287	-0.00355	-0.0854	--
107	2018-02-05	2.43	2.94	269	876	2.44	276	-0.00908	-0.2	--
108	2018-03-05	2.52	2.98	331	960	2.47	294	0.0527	1.22	--
109	2018-03-20	2.35	2.91	222	812	2.42	261	-0.0689	-1.51	--
110	2018-04-16	2.48	3.01	302	1010	2.48	306	-0.00438	-0.124	--
111	2018-04-30	2.46	2.98	287	962	2.47	295	-0.00992	-0.239	--
112	2018-05-15	2.38	2.8	238	638	2.34	220	0.0358	0.785	--
113	2018-05-29	2.41	2.93	260	843	2.43	268	-0.012	-0.298	--
114	2018-06-11	2.47	3.1	293	1250	2.55	355	-0.0812	-1.81	--
115	2018-06-25	2.45	2.93	284	854	2.43	271	0.0224	0.57	--
116	2018-07-16	2.53	3.13	336	1350	2.57	376	-0.047	-1.22	--
117	2018-08-21	2.39	2.8	248	636	2.34	220	0.0546	1.31	--
118	2018-10-11	2.06	2.48	114	303	2.11	130	-0.0535	-1.4	--
119	2018-11-29	2.26	2.68	180	483	2.25	181	0.000594	-0.00948	--
120	2018-12-18	2.3	2.78	198	596	2.32	210	-0.023	-0.638	--
121	2019-02-06	2.47	2.9	293	799	2.41	258	0.0564	1.4	--
122	2019-03-06	2.48	2.92	300	828	2.42	265	0.0557	1.35	--
123	2019-03-19	2.39	2.85	247	714	2.38	238	0.0171	0.44	--
124	2019-04-01	2.46	2.95	291	892	2.44	279	0.0195	0.526	--
125	2019-04-16	2.58	3.02	380	1050	2.5	314	0.0843	2.06	--
126	2019-05-09	2.1	2.48	126	304	2.11	130	-0.0111	-0.278	--
127	2019-05-20	2.33	2.76	215	569	2.31	203	0.0271	0.661	--
128	2019-06-03	2.26	2.65	182	449	2.23	171	0.028	0.709	--
129	2019-06-26	2.2	2.62	158	421	2.21	164	-0.0135	-0.44	--
130	2019-07-16	2.3	2.75	201	556	2.3	200	0.00479	0.104	--

| 131 | 2019-08-20 | 2.24 | 2.73 | 174 | 533 | 2.29 | 194 | -0.0446 | -1.04 | -- |
| 132 | 2019-09-24 | 2.52 | 3 | 334 | 999 | 2.48 | 303 | 0.0442 | 1.01 | -- |

Definitions

CaCO3: Total hardness, in milligrams per liter as calcium carbonate (00900).

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

DFFITS: 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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