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An Evaluation of Water-Quality Records for Texas Streams

BLAKEY et al

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY - WATER RESOURCES DIVISION

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By J. F. Blakey, R. O. Hawkinson, and T. D. Steele

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By

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ABSTRACT

Chemical data for 12 streamflow-sampling stations in Texas, each having from 8 to 24 years of available historical records, were analyzed to determine functional relationships between concentrations of the major inorganic constituents and specific conductance or stream discharge. Regression equations for each station were derived by using data for an identical 5-year period; the remaining record served as independent test data for checking the adequacy of the functions on the basis of continued specific-conductance determinations as an index variable.

Daily solute concentrations and loads at a sampling site were simulated, and monthly and annual averages were computed by using daily records of specific conductance in conjunction with the regression equations. Simulated annual mean concentrations of most individual solutes and dissolved solids averaged within 10-20 percent of comparable concentrations determined from the composited chemical analyses, although systematic biases were detected in results for some of the relationships used in the simulation. Results of the evaluation of the 12 stations indicated that regression equations, using specific conductance as the independent variable, can be used as an alternative to composite analyses for calculation of solute concentrations and loads in Texas streams and is a flexible system that can be applied with sufficient accuracy to satisfy most anticipated needs for data.

INTRODUCTION

Ever increasing efforts to stop or reduce pollution and to develop water supplies result in a growing demand for current and applicable water-quality data. To provide this information, data-collection activities must be designed and periodically reviewed in relation to data requirements and uses.

For many years, the U.S. Geological Survey has placed major emphasis on collecting data on inorganic constituents. However, in the mid-sixties, the Survey began a shift in emphasis to organic-and biochemical-data collection. This change was necessary to provide action agencies with information on environmental quality. In re-directing efforts, the Survey has reviewed and continues to review data-collection activities in relation to data-users' needs. Limitations of funds and manpower, however, often require reducing one phase of the data-collection program in order to add others.

Statistical techniques in analysis of historical inorganic chemical-quality records are available to supplement judgment decisions for modifying data-collection activities. Large volumes of historical records can be analyzed with a sequence of computer programs to determine statistical properties of each constituent and, where applicable, to develop a regression relationship between each water-quality variable and streamflow or specific conductance. Additional computer programs in the sequence can be used to simulate water-quality records, to make time-trend analyses, and to regionalize water-quality conditions.

This study has the following purposes:

(1) To analyze, by statistical techniques, historical records of inorganic chemical quality of water at points on selected Texas streams;

(2) to present results from the computer-oriented analyses and to describe their usefulness as tools in data evaluation and network design; and

(3) to determine the accuracy with which inorganic chemical constituents can be estimated in a reduced data-collection program by using specific conductance or stream discharge as an index variable.

AVAILABLE RECORDS

Historical records of chemical quality for 12 Texas stations were selected for analysis. All 12 streams were operated as daily sampling stations during the 1960-69 water years, and they represent a cross-section of geologic and hydrologic conditions in Texas. Records of specific conductance for periods of more than 20 years were available and were used in the analyses for four stations. Station information is summarized in table 1 and station locations are shown on figure 1.

Figure 1 (caption on next page) belongs near here.

All chemical analyses in the data sets are for composited samples, except for a few discrete samples obtained during periods of high runoff. Composited samples consist of from two to 31 daily samples of "similar" specific conductance. Daily records of specific conductance and stream discharge were used in conjunction with the data sets for all stations

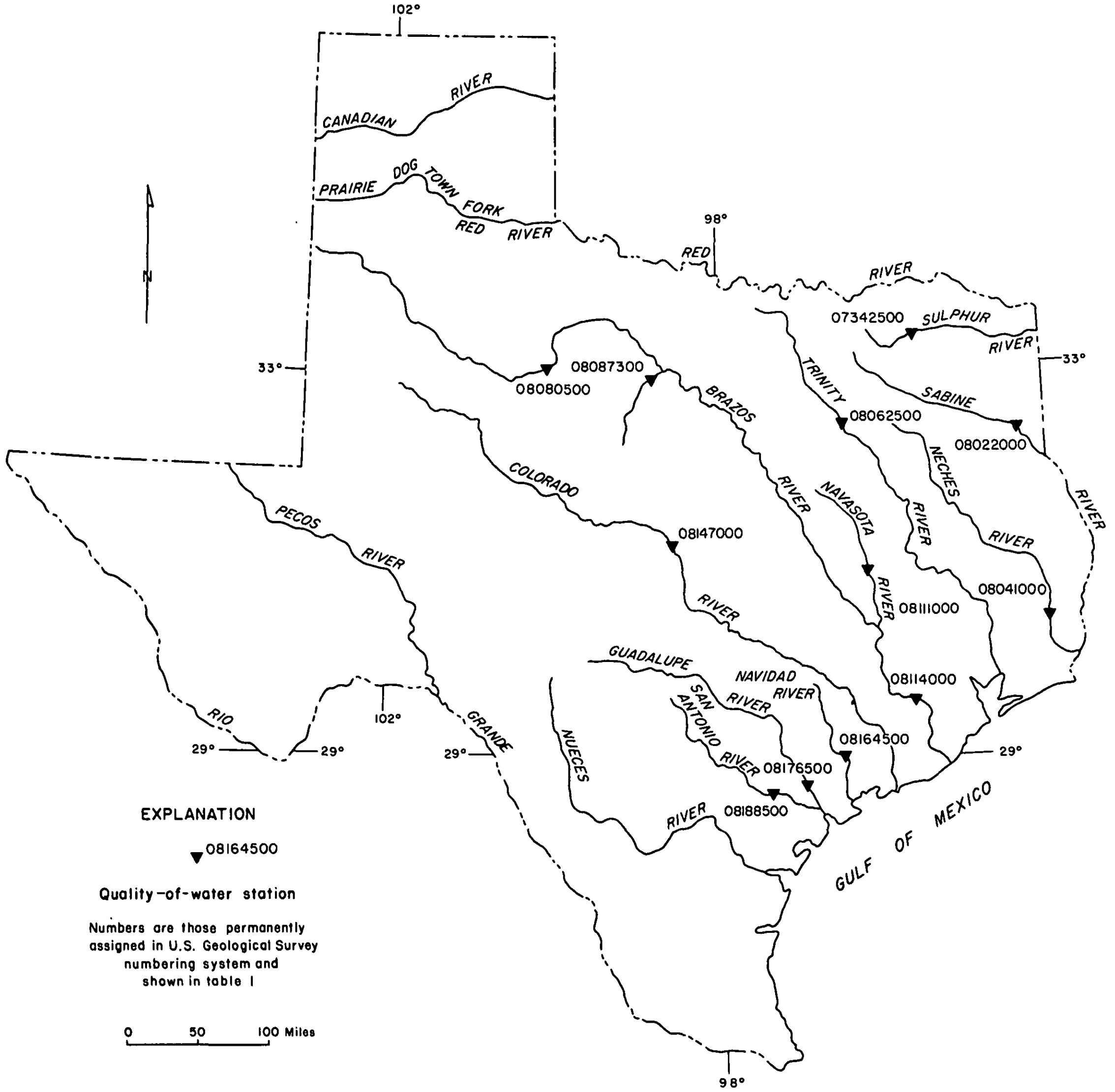


FIGURE 1 – Locations of water-quality stations used in the evaluation study

Table 1.--Summary of the 12 chemical-quality sampling stations selected for the Texas study

USGS station number	Location	Drainage area (sq. mi.)	Period of record 1/ (water years)	Number of years	Number of analyses 2/
07342500	South Sulphur River near Cooper	527	1960-66, 68-69	9	194
08022000	Sabine River near Tatum	3,586	1960-69	10	190
08041000	Neches River at Evadale 3/	7,923	1948-69	22	148
08062500	Trinity River near Rosser	8,162	1960-69	10	169
08080500	Double Mountain Fork Brazos River near Aspermont	7,980	1960-69	10	198
08087300	Clear Fork Brazos River at Eliasville	5,721	1962-69	8	187
08111000	Navasota River near Bryan	1,439	1960-69	10	226
08114000	Brazos River at Richmond 3/	44,020	1946-69	24	189
08147000	Colorado River near San Saba 3/	30,600	1948-69	22	174
08164500	Navidad River near Ganado	1,116	1960-69	10	222
08176500	Guadalupe River at Victoria 3/	5,161	1946-69	24	136
08188500	San Antonio River at Goliad	3,918	1960-69	10	186
Totals:				169	2,219 4/

1/ Period of record used for analysis, not necessarily including all data for the station.

2/ Number of composited analyses for 1962-66 water years only, the period used for regression analysis.

3/ Selected for analyses of long-term records (20 years or longer).

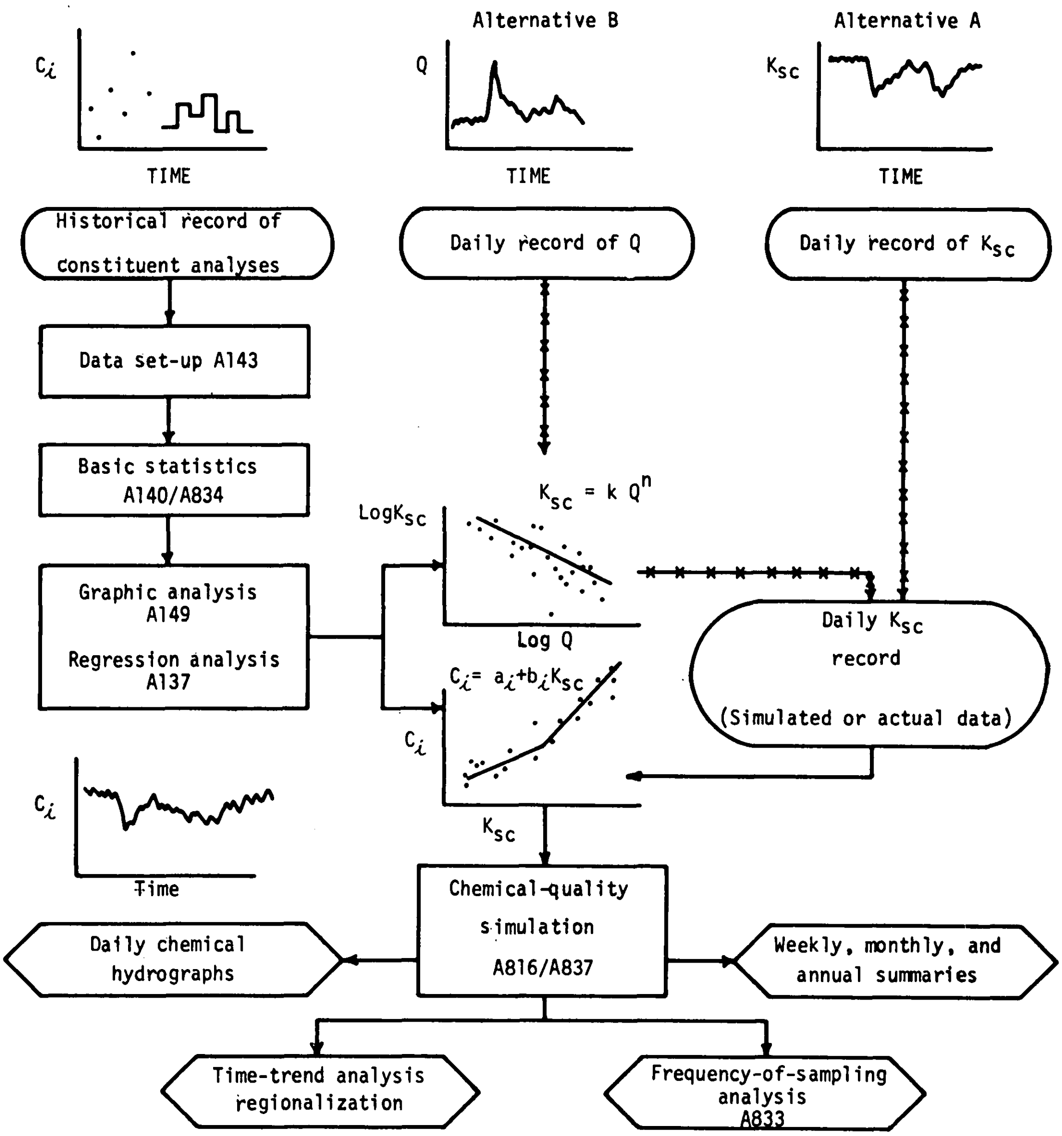
4/ A total of 4,515 composited analyses were available for 1960-69 water years.

METHODS OF EVALUATION

Historical records of chemical analyses for the 12 stations were analyzed with a sequence of computer programs developed by Steele (1970, 1971). A flow chart showing the procedures utilized in the data analysis and simulation is shown in figure 2.

Figure 2 (caption on next page) belongs near here.

All inorganic chemical analyses of samples from the 12 stations for the 1960-69 period were retrieved from the Geological Survey's "National water data storage and retrieval system," using the data set-up computer program. The basic statistics of the data set for each station were computed and printouts were examined to determine the number of data items and the range in concentration for each constituent in preparing for the graphic analysis.



Explanation

C_i : Concentration of chemical constituent where i = specific constituents.
Q : Discharge.
K_{sc}: Specific conductance.
k : Regression constant for log K_{sc}-log Q relationship.
n : Regression coefficient for log K_{sc}-log Q relationship.
a_i : Regression constant for arithmetic relationship between K_{sc} and C_i .
b_i : Regression coefficient for arithmetic relationship between K_{sc} and C_i .

(Adapted from Steele, 1970, p. 348)

Figure 2.--Flow chart showing procedures for data analysis and simulation.

In the graphic analysis, all inorganic constituents (C_i) were considered dependent variables and were plotted against discharge (Q), using logarithmic coordinates, and against specific conductance (K_{sc}), using cartesian coordinates. The graphic display serves two important functions in the data evaluation: (1) Transcriptional errors and outliers are detected and checked; and (2) nonlinearity in a given dependent-independent variable relationship in the data set is readily detected. Anomalies in the data set can be corrected or omitted, and nonlinear relationships can be partitioned before the development of regression equations.

After examining the graphic analyses and making any necessary adjustments in each data set, regression equations were developed for C_i-K_{sc} relationships. Chemical analyses from identical 5-year periods (water years 1962-66) for each station were used as the calibration period for development of the relationships.

The regression equations were then used in conjunction with records of daily specific conductance and daily mean discharge to simulate inorganic-chemical data for the entire period of record available for each station (table 1). Records were simulated for a total of 169 station years, of which 109 years represented independent test data.

DISCUSSION OF RESULTS

Graphic analyses of C_i-Q (and K_{sc}-Q) generally showed poor relationships, if any, between concentration and discharge for all stations. Typical plots of dissolved-solids concentration versus discharge for stations used in the study are shown on figures 3a and 3b. These results coincide with the findings of many other investigators who have reported the poor correlation of C_i-Q in streams in Texas and other western states (Rawson, 1967, p. 25; Colby, Hembree, and Rainwater, 1956, p. 123; Leifeste, Blakey, and Hughes, 1971, p. 12; Steele, 1970, p. 349). On the other hand, C_i-K_{sc} regression results were generally quite good, with high correlations and relatively low standard errors of estimate.

Figures 3a and 3b (captions on next page) belong near here.

The basic statistics for all stations are summarized in table 2, and the regression equations for C_i-K_{sc} relationships are shown in table 3. Also shown in table 3 is the range in K_{sc} over which the regression equations are applicable. Where negative intercept values (a_i) resulted from fitting a straight line to slightly curvilinear C_i-K_{sc} relationships, the lower limits of the range in K_{sc} have been adjusted upward to prevent calculation of negative concentrations. Constituents and variables in the tables are expressed in mg/l (milligrams per liter) except Q (cubic feet per second), SC (micromhos per centimeter), and pH (units)--abbreviations are Q (stream discharge), HRD (hardness), NCH (non-carbonate hardness), DS (dissolved solids), and SC (specific conductance). Examples of C_i-K_{sc} plotted data for 1962-66 water years used in the regression analysis are shown on figures 4a and 4b to 6a and 6b.

Figures 4a, 4b, 5a, 5b, 6a, and 6b (captions on next page) belong near here.

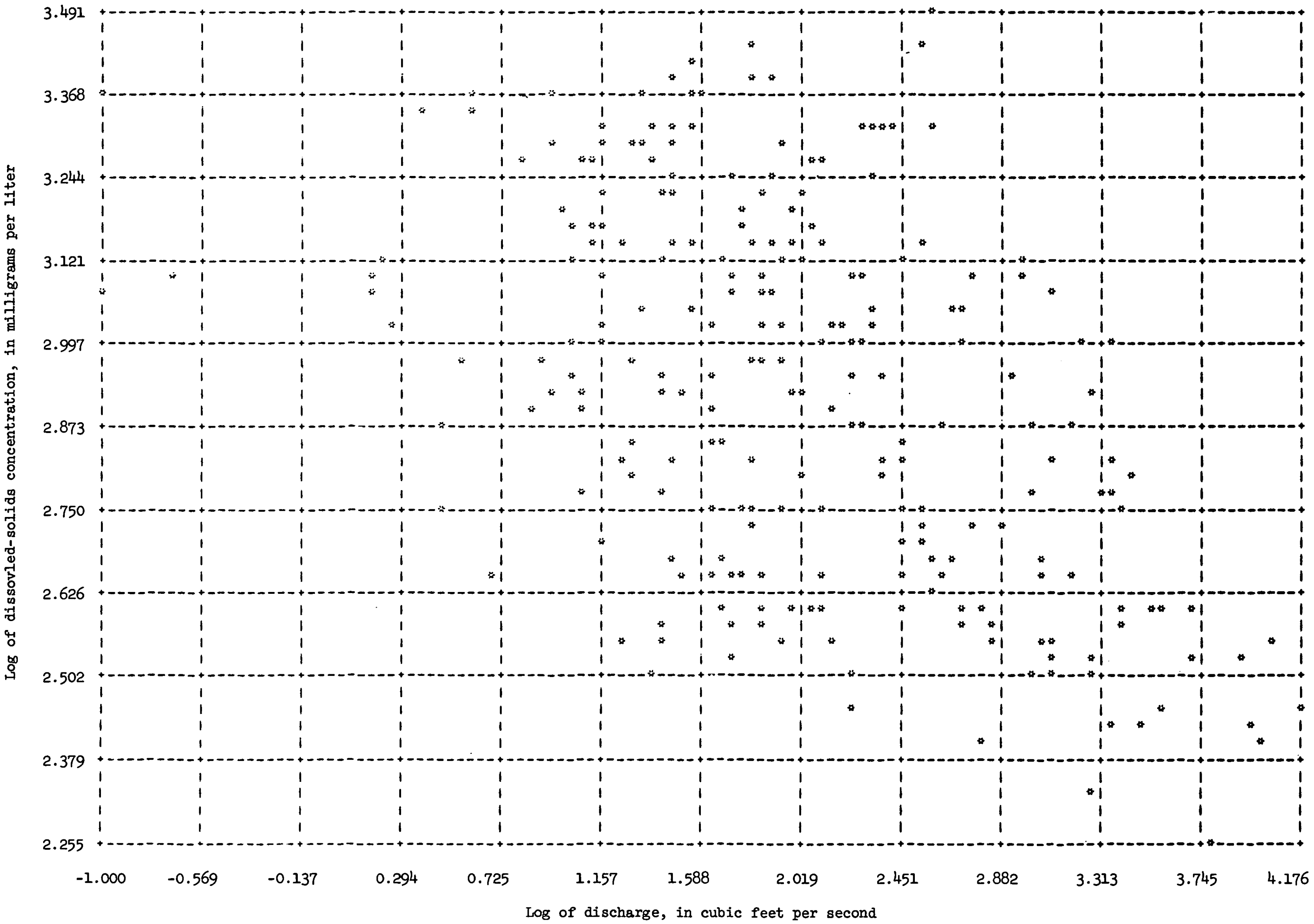


Figure 3a.--Dissolved solids versus discharge for station 08087300, Clear Fork Brazos River at Eliasville, Tex.

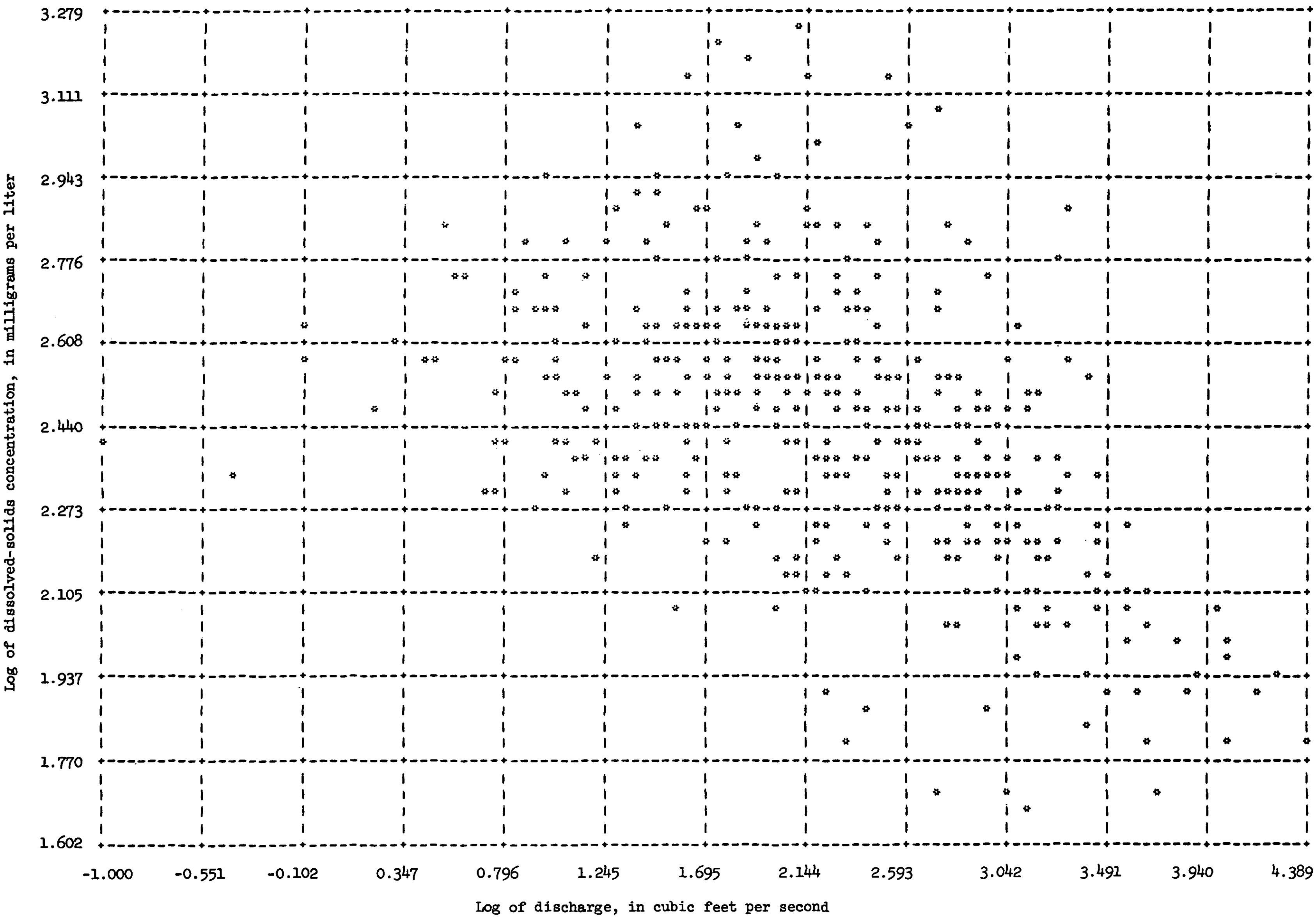


Figure 3b.--Dissolved solids versus discharge for station 08111000, Navasota River near Bryan, Tex.

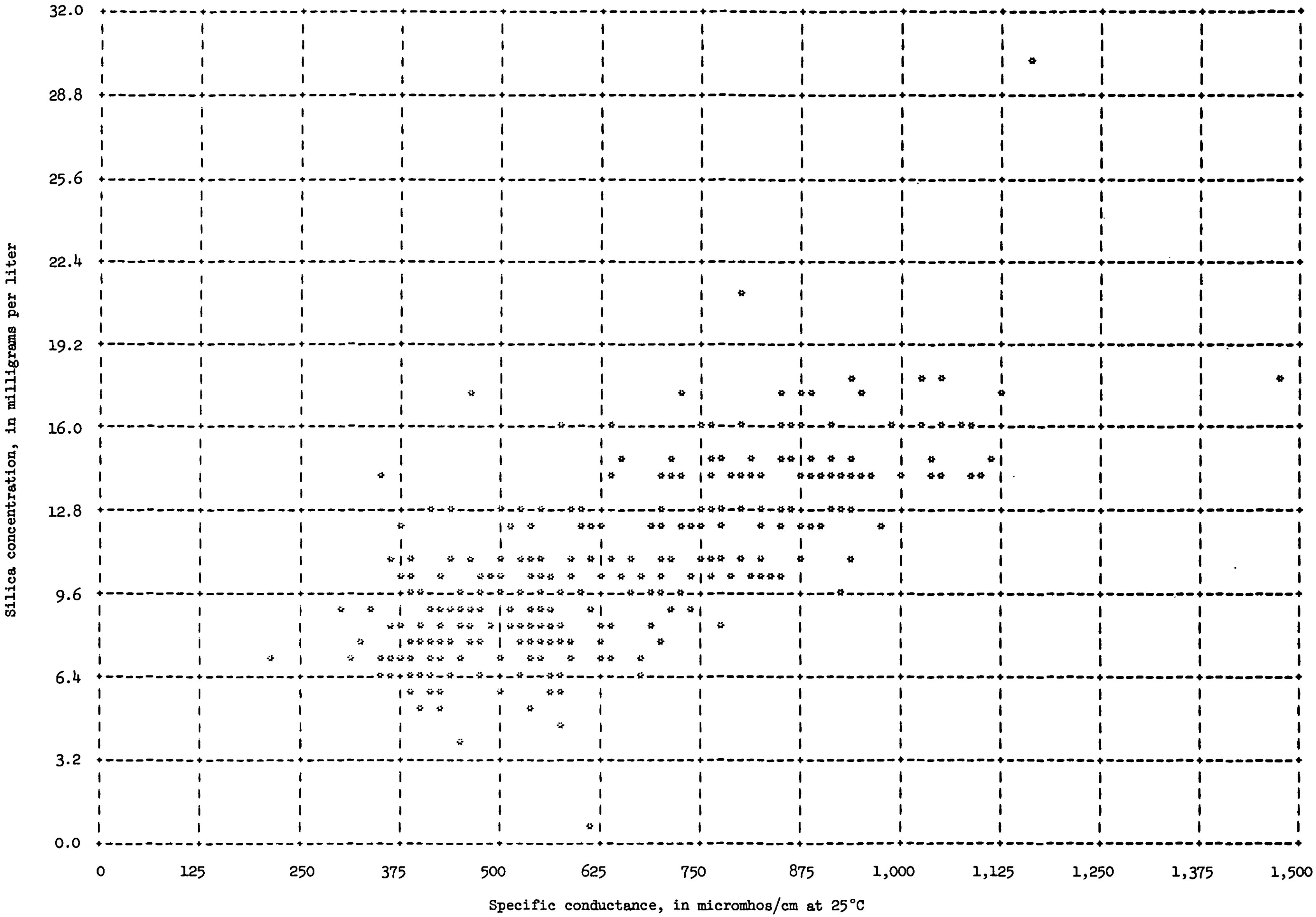


Figure 4a.--Silica versus specific conductance for station 08062500, Trinity River near Rosser, Tex.

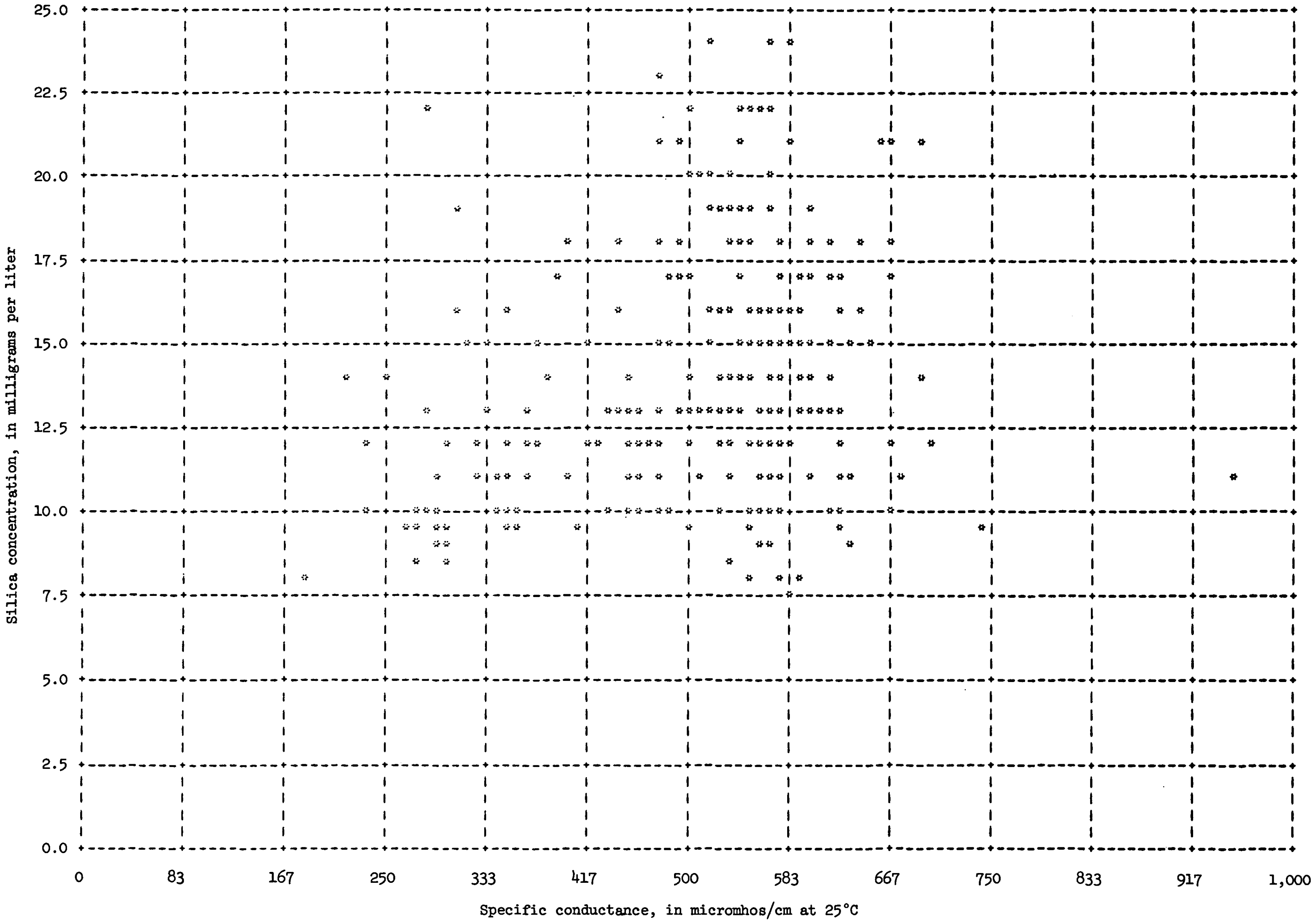


Figure 4b.--Silica versus specific conductance for station 08176500, Guadalupe River at Victoria, Tex.

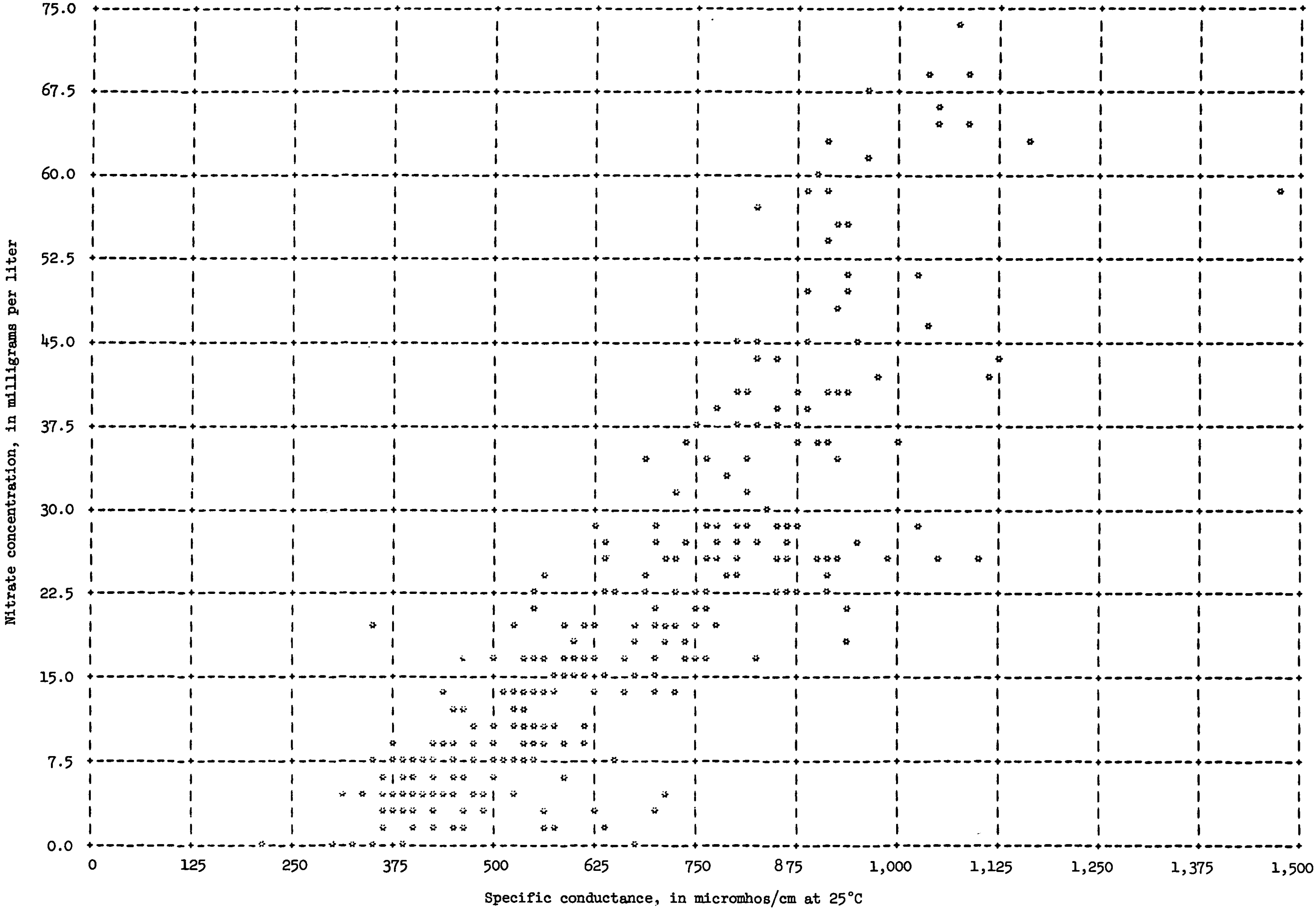
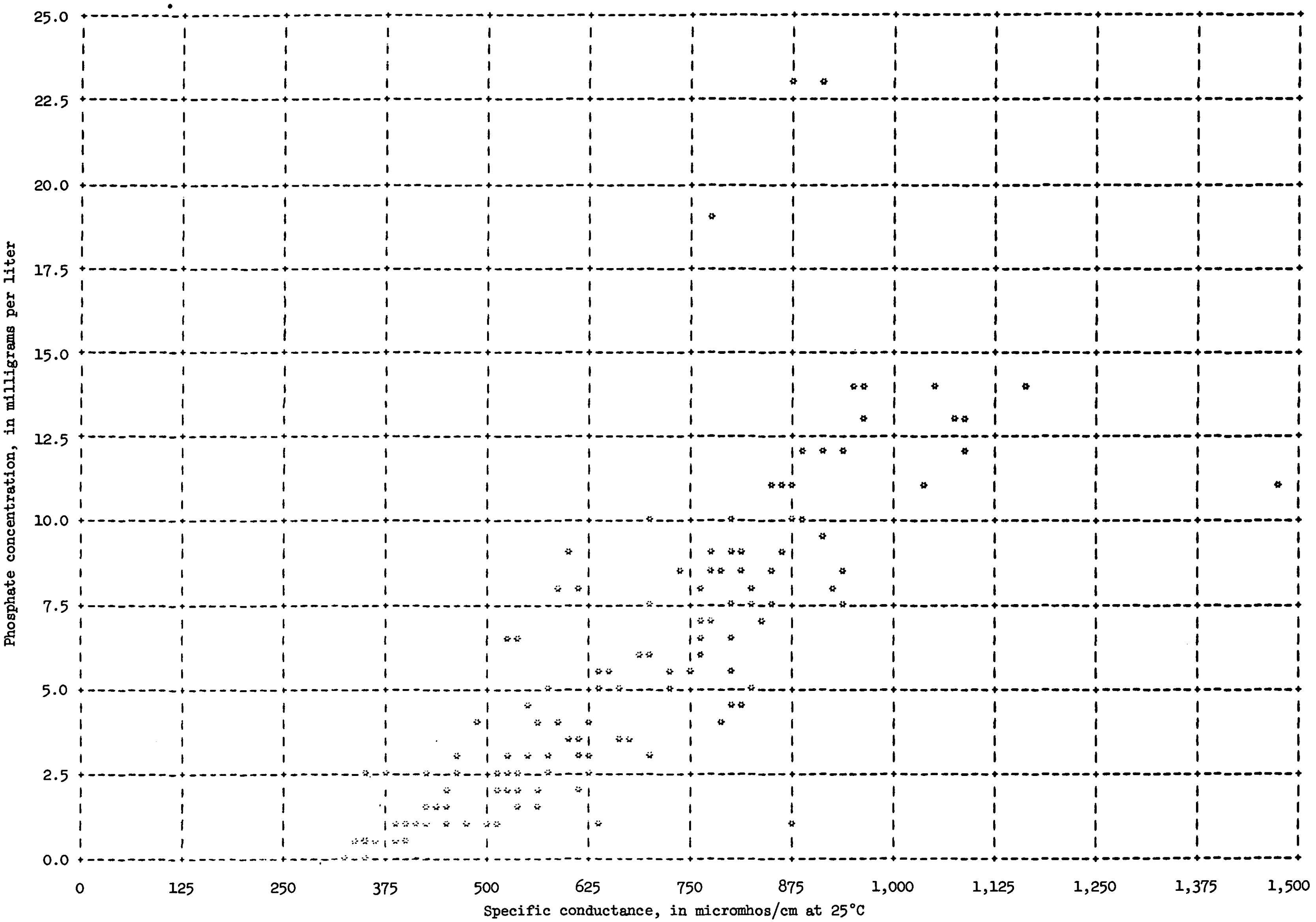


Figure 5a.--Nitrate versus specific conductance for station 08062500, Trinity River near Rosser, Tex.



All stations have been processed

Figure 5b.--Phosphate versus specific conductance for station 08062500, Trinity River near Rosser, Tex.

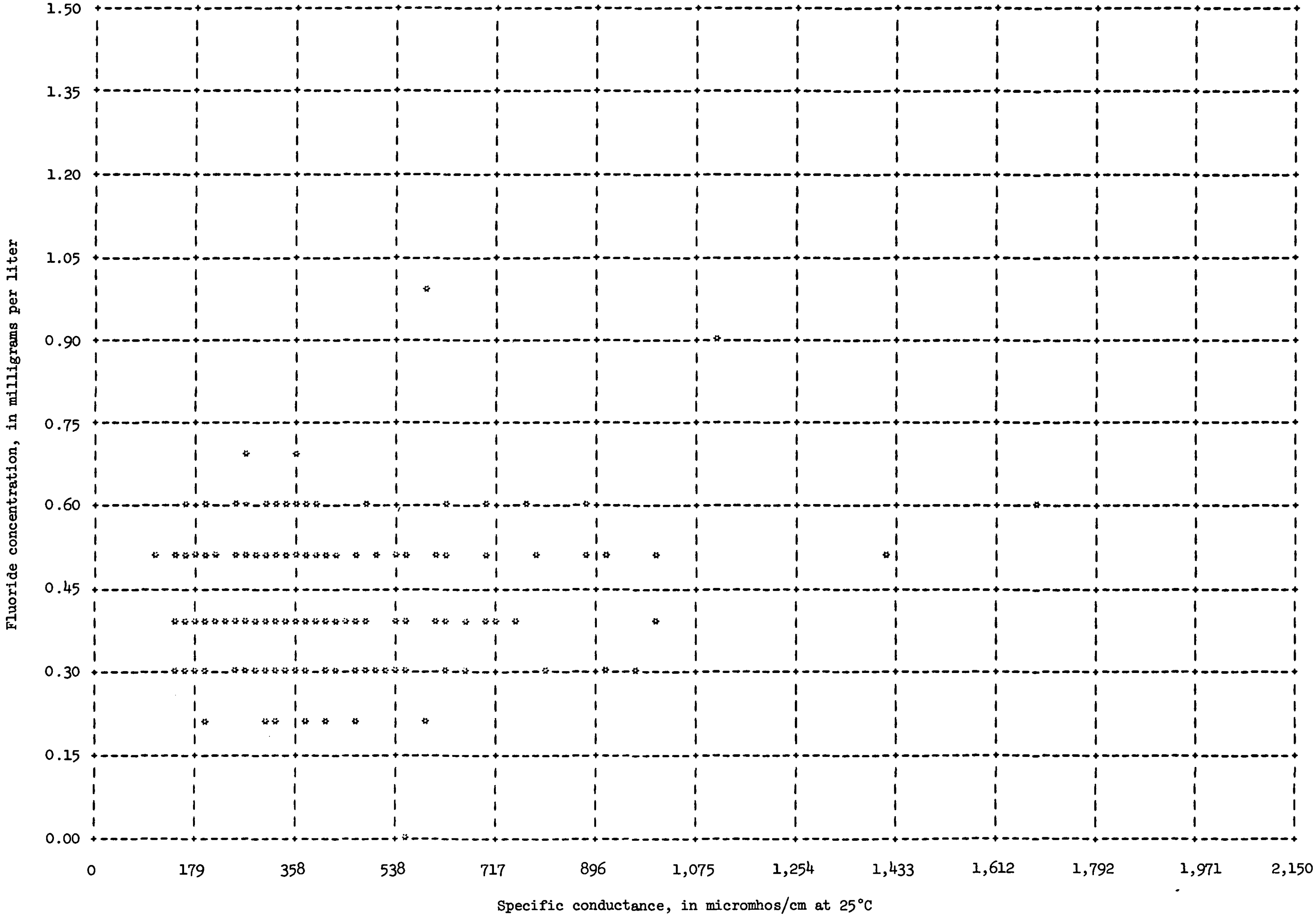


Figure 6a.--Fluoride versus specific conductance for station 07342500, South Sulphur River near Cooper, Tex.

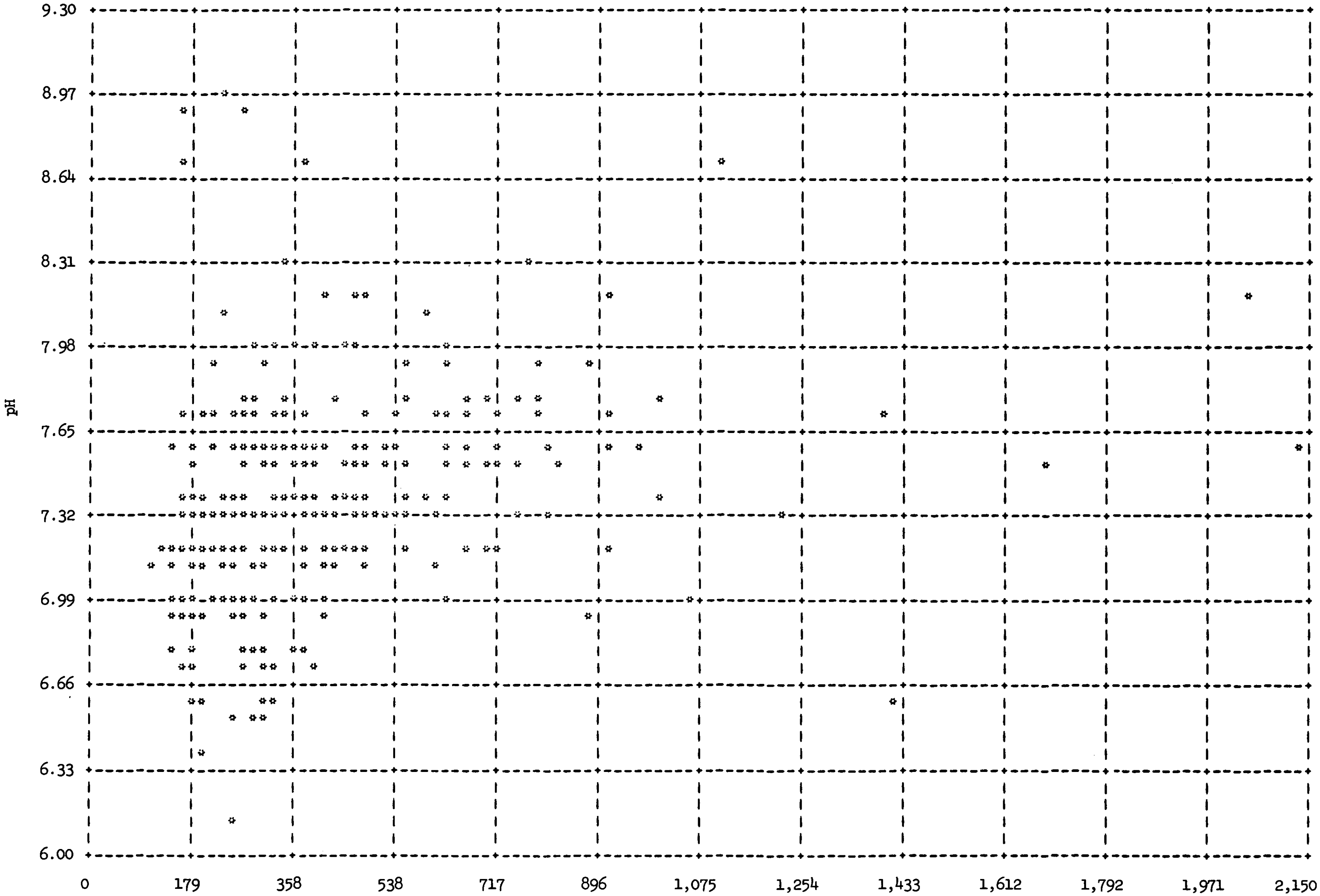


Figure 6b.--pH versus specific conductance for station 07342500, South Sulphur River near Cooper, Tex.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years

(Constituents in milligrams per liter except as indicated)

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
07342500 SOUTH SULPHUR RIVER NEAR COOPER, TEX.						
[a] Q	707	2313	194	23,900	0.20	7.45
SiO_2	10.8	3.48	175	22	.0	.19
Ca	45.9	21.1	167	116	17	1.13
Mg	5.02	2.64	167	14	1.1	1.18
Na	35.8	38.8	175	326	4.4	3.94
K	3.67	.86	49	6.9	2.3	1.07
HCO_3	155	72.2	194	403	43	1.01
SO_4	35.3	22.4	194	111	8.2	1.74
Cl	29.0	56.3	194	580	1.6	6.65
DS	250	151	167	1,150	84	2.25
[b] SC	406	254	194	2,130	124	2.65
HRD	129	62.0	194	347	16	1.17
NCH	8.73	18.8	194	153	0	5.03
F	.42	.12	97	.9	.0	.26
[c] pH	7.33	.45	191	9.0	6.1	.79
NO_3	1.92	2.05	182	13	.0	3.14
08022000 SABINE RIVER NEAR TATUM, TEX.						
[a] Q	1590	3884	190	37,720	32	6.57
SiO_2	12.7	3.78	186	19	1.1	-.65
Ca	16.2	4.88	186	34	5.2	.64
Mg	5.89	1.85	186	14	1.0	.85
Na	84.2	55.9	186	574	12	4.05
K	3.72	.66	42	5.6	2.1	.43
HCO_3	35.3	18.6	190	90	10	.87
SO_4	35.3	14.6	190	105	8.0	1.20
Cl	128	84.7	190	880	18	4.13
DS	303	156	188	1,610	61	3.48
[b] SC	567	302	190	3,040	104	3.34
HRD	64.1	18.3	190	124	15	.39
NCH	35.3	17.8	190	92	1	.66
F	.23	.07	78	.4	.1	.12
[c] pH	6.52	.38	190	7.6	5.6	.38
NO_3	1.21	1.01	188	7.1	.0	2.05

See footnotes at end of table.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years--continued

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
08041000 NECHES RIVER AT EVADALE, TEX.						
a/ Q	4176	4702	148	20,680	168	1.91
SiO_2	12.8	3.22	148	22	.0	-.40
Ca	9.30	2.50	148	16	2.5	-.24
Mg	3.29	.97	148	6.3	.0	-.12
Na	23.5	9.49	148	59	2.3	.58
K	2.81	.79	37	3.8	.9	-.77
HCO_3	29.4	13.0	147	72	6.0	.64
SO_4	18.8	6.15	147	34	2.8	.49
Cl	31.0	12.2	147	72	2.0	.41
DS	115	34.2	145	218	14	-.02
b/ SC	198	61.1	145	397	29	.14
HRD	36.8	9.67	145	61	6	-.46
NCH	12.4	6.38	145	28	0	.60
F	.18	.08	87	.4	.0	-.32
c/ pH	6.53	.45	145	8.6	5.7	1.06
NO_3	.69	.42	145	3.8	.0	2.96
PO_4	.04	.03	17	.08	.00	-.07
08062500 TRINITY RIVER NEAR ROSSER, TEX.						
a/ Q	2849	5412	169	42,000	235	4.34
SiO_2	11.2	3.56	164	30	.5	.94
Ca	53.7	8.60	165	73	21	-.47
Mg	5.35	1.89	165	14	1.6	1.20
Na	76.6	43.2	164	253	13	.66
K	7.99	3.33	51	17	3.8	.63
HCO_3	157	22.6	169	211	58	-.72
SO_4	88.2	44.0	168	424	25	2.69
Cl	56.6	28.2	169	120	7.8	.21
DS	403	140	166	975	112	.50
b/ SC	668	215	169	1470	210	.35
HRD	156	22.5	169	200	64	-.52
NCH	26.5	14.5	169	98	0	1.00
F	.74	.35	82	2.3	.2	1.35
c/ pH	7.26	.42	169	8.8	6.5	.70
NO_3	22.5	17.1	164	74	.0	.91
PO_4	5.27	4.11	105	14	.05	.53

See footnotes at end of table.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years--continued

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
08080500 DOUBLE MOUNTAIN FORK BRAZOS RIVER NEAR ASPERMONT, TEX.						
a/ Q	225	730	198	7,250	0.10	6.43
SiO_2	12.8	3.34	178	22	.4	-.11
Ca	466	234	180	920	73	.17
Mg	74.1	49.6	179	209	8.8	.61
Na	596	355	183	1,360	33	.15
K	9.02	2.82	44	14	4.9	.15
HCO_3	103	22.3	195	176	61	.49
SO_4	1213	550	197	2,120	221	.02
Cl	976	657	198	2,300	58	.25
DS	3408	1814	182	6,470	599	.09
b/ SC	4713	2384	197	9,180	930	.14
HRD	1441	754	195	2,960	232	.31
NCH	1356	756	195	2,900	125	.30
F	.65	.29	43	1.7	.3	1.62
c/ pH	7.30	.29	194	7.9	6.3	-.37
NO_3	1.69	1.36	176	10	.0	1.77
08087300 CLEAR FORK BRAZOS RIVER AT ELIASVILLE, TEX.						
a/ Q	744	1842	187	12,100	0.10	4.19
SiO_2	7.03	3.06	173	20	.4	.82
Ca	100	51.2	175	255	37	1.15
Mg	33.5	25.4	175	159	4.4	1.57
Na	191	140	173	627	20	1.05
K	6.84	1.62	47	9.9	3.8	-.13
HCO_3	135	34.4	187	245	42	.52
SO_4	161	165	186	912	12	2.01
Cl	366	278	187	1,420	42	1.29
DS	947	618	177	3,020	180	1.05
b/ SC	1639	1000	187	4,810	338	1.00
HRD	384	226	187	1,290	110	1.31
NCH	273	211	187	1,180	24	1.41
F	.30	.08	92	.5	.0	-.31
c/ pH	7.33	.32	187	8.7	6.5	.47
NO_3	2.26	1.28	173	7.6	.0	1.00

See footnotes at end of table.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years--continued

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
			08111000 NAVASOTA RIVER NEAR BRYAN, TEX.			
[a] Q	723	2469	226	24,100	0.10	6.69
SiO_2	12.7	3.2	205	22	5.3	.20
Ca	29.2	14.6	206	82	5.5	1.04
Mg	7.8	3.8	206	21	1.3	.91
Na	91.5	90.3	206	606	6.7	2.98
K	4.09	.64	50	5.7	2.6	.23
HCO_3	61.0	26.1	226	136	13	.68
SO_4	37.7	18.6	226	94	6.6	.74
Cl	156	160	226	1,020	4.8	2.72
DS	374	276	224	1,810	49	2.33
[b] SC	692	524	226	3,370	79	2.32
HRD	107	53	226	288	19	.95
NCH	57	42	226	230	1.0	1.46
F	.27	.10	88	.5	.0	.08
[c] pH	6.94	.32	225	7.7	6.3	.34
NO_3	.92	.74	204	4.2	.0	1.66
			08114000 BRAZOS RIVER AT RICHMOND, TEX.			
[a] Q	7743	13159	189	90,580	312	3.90
SiO_2	10.4	2.62	183	18	4.4	.69
Ca	62.6	16.1	182	107	32	.37
Mg	11.1	4.49	182	25	3.3	.66
Na	77.1	48.0	183	233	12	1.02
K	3.91	.59	35	5.3	2.6	.26
HCO_3	156	30.5	189	254	87	.22
SO_4	77.3	42.1	189	224	21	.97
Cl	111	73.8	189	362	8.7	1.06
DS	434	194	184	1,040	154	.83
[b] SC	754	328	189	1,830	257	.86
HRD	200	57.7	189	370	97	.45
NCH	72.0	44.9	189	227	10	1.05
F	.34	.09	80	.50	.0	-1.37
[c] pH	7.4	.52	189	8.1	6.8	.49
NO_3	1.63	1.06	183	7.3	.0	1.31
PO_4	.11	.08	25	.29	.00	.33

See footnotes at end of table.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years--continued

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
			08147000 COLORADO RIVER NEAR SAN SABA, TEX.			
[a] Q	1291	3077	174	26,410	0.10	6.01
SiO_2	9.39	2.66	162	19	3.9	1.04
Ca	63.0	20.5	162	202	32	2.83
Mg	21.6	11.8	162	82	3.3	1.45
Na	68.9	59.4	162	564	6.0	4.22
K	4.14	.89	41	7.4	2.6	1.51
HCO_3	199	46.1	174	314	112	.43
SO_4	65.4	60.4	170	500	7.0	3.59
Cl	126	119	174	1,000	3.4	3.44
DS	460	270	164	2,440	149	3.29
[b] SC	834	473	174	4,120	262	2.91
HRD	249	95.1	174	842	102	2.24
NCH	86.2	90.8	174	708	0	3.40
F	.30	.09	79	.7	.1	.89
[c] pH	7.44	.33	174	8.2	6.6	0
NO_3	1.63	1.27	162	6.8	.0	1.00
			08164500 NAVIDAD RIVER NEAR GANADO, TEX.			
[a] Q	543	1040	222	7,079	3.5	3.77
SiO_2	19.0	8.50	219	49	5.7	1.12
Ca	43.6	21.7	212	100	8.5	.51
Mg	6.27	3.69	212	21	1.4	1.44
Na	39.7	22.5	217	138	3.0	.91
K	3.51	.94	67	6.4	2.4	1.61
HCO_3	157	72.6	218	326	34	.24
SO_4	14.8	5.74	222	37	4.0	.82
Cl	53.6	30.9	222	170	3.8	.60
DS	256	118	221	614	63	.27
[b] SC	448	201	222	1,020	106	.18
HRD	134	61.5	218	274	26	.23
NCH	6.46	7.96	218	57	0	2.59
F	.34	.11	116	.7	.1	.29
[c] pH	7.35	.39	216	8.5	6.2	-.23
NO_3	.95	.74	219	3.5	.0	1.04
PO_4	.06	.07	29	.34	.00	2.72

See footnotes at end of table.

Table 2. Basic statistics of water-quality data sets from 12 Texas stations 1962-66 water years--continued

Constituent	Mean	Standard deviation	Sample size	Maximum observed	Minimum observed	Skewness
08176500 GUADALUPE RIVER AT VICTORIA, TEX.						
a/ Q	1597	1941	136	10,360	165	2.57
SiO_2	13.8	3.62	134	24	7.3	.58
Ca	54.6	10.8	133	80	27	-.10
Mg	13.7	4.52	132	25	2.9	-.59
Na	28.7	8.98	134	53	5.3	.02
K	3.01	.87	33	5.6	2.1	1.43
HCO_3	202	56.4	136	282	107	--
SO_4	28.4	6.98	134	46	7.4	-.07
Cl	38.6	12.9	134	78	5.7	.06
DS	286	61.1	133	432	133	-.69
b/ SC	493	101	136	695	217	-.78
HRD	192	41.0	134	272	90	-.60
NCH	22.9	10.9	134	55	0	.14
F	.30	.07	79	.5	.1	-.05
c/ pH	7.54	.31	135	8.4	6.6	.26
NO_3	2.58	1.15	135	5.8	.0	.16
08188500 SAN ANTONIO RIVER AT GOLIAD, TEX.						
a/ Q	663	1004	186	8129	48	4.11
SiO_2	17.4	3.78	170	27	10	.14
Ca	77.2	20.6	169	110	29	-.48
Mg	15.7	6.03	169	26	2.3	-.40
Na	69.4	28.4	171	132	13	-.28
K	6.30	1.24	42	8.9	2.4	-1.09
HCO_3	229	63.3	186	324	89	-.42
SO_4	77.1	31.3	185	142	8.6	-.40
Cl	85.4	39.8	186	182	11	-.16
DS	480	159	170	761	130	-.45
b/ SC	777	264	186	1290	218	-.41
HRD	248	80.6	186	372	44	-.42
NCH	60.9	29.0	186	122	0	-.23
F	.50	.13	97	.8	.1	-.39
c/ pH	7.67	.29	186	8.4	6.9	-.35
NO_3	8.99	4.28	162	22	.2	.40
PO_4	2.70	1.94	21	8.0	.45	1.47

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a/ Cubic feet per second.
b/ Micromhos per centimeter.
c/ Units.

Table 3. Results of regression analyses, $C_i = a_i + b_i K_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water years

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
07342500 SOUTH SULPHUR RIVER NEAR COOPER, TEX.									
Ca	167	18.27	0.0651	45.9	21.1	0.80	12.6	27	110 - 2200
Mg	167	1.73	.0078	5.02	2.64	.77	1.69	34	110 - 2200
Na	175	-22.66	.1408	35.8	38.8	.94	13.6	38	170 - 2200
K	49	2.66	.0028	3.67	.86	.61	.69	19	110 - 2200
HCO_3	194	70.67	.2072	155	72.2	.73	49.6	32	110 - 2200
SO_4	194	9.79	.0628	35.3	22.4	.71	15.8	45	110 - 2200
Cl	194	-46.78	.1867	29.0	56.3	.84	30.4	105	255 - 2200
DS	167	8.37	.5723	250	151	.99	17.1	7	110 - 2200
HRD	194	48.78	.1981	129	62.0	.81	36.3	28	110 - 2200
08022000 SABINE RIVER NEAR TATUM, TEX.									
Ca	185	9.01	0.0127	16.1	4.71	0.65	3.60	22	100 - 3100
Mg	185	3.14	.0049	5.87	1.84	.64	1.41	24	100 - 3100
Na	186	-20.83	.1838	84.2	55.9	.99	6.81	8	115 - 3100
K	41	2.93	.0013	3.70	.65	.46	.58	16	100 - 3100
HCO_3	190	24.77	.0185	35.3	18.6	.29	17.8	50	100 - 3100
SO_4	190	18.09	.0304	35.3	14.6	.63	11.3	32	100 - 3100
Cl	190	-29.78	.2776	128	84.7	.99	12.8	10	110 - 3100
DS	188	9.99	.5154	303	156	.99	10.1	3	100 - 3100
HRD	190	39.85	.0428	64.1	18.3	.70	13.1	20	100 - 3100

Table 3. Results of regression analyses, $C_i = a_i + b_iK_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water years--Continued

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
08041000 NECHES RIVER AT EVADALE, TEX.									
Ca	145	2.21	0.0358	9.30	2.49	0.88	1.20	13	25 - 410
Mg	145	.98	.0117	3.30	.97	.73	.66	20	25 - 410
Na	145	-5.98	.1488	23.5	9.43	.96	2.48	11	42 - 410
K	35	1.64	.0068	2.81	.81	.53	.69	25	25 - 410
HCO_3	145	-2.59	.1627	29.7	13.0	.76	8.36	28	25 - 410
SO_4	145	9.25	.0481	18.8	6.18	.47	5.46	29	25 - 410
Cl	145	-7.70	.1960	31.1	12.3	.98	2.59	8	42 - 410
DS	145	5.67	.5534	115	34.2	.99	5.22	5	25 - 410
HRD	145	9.34	.1384	36.8	9.67	.87	4.69	13	25 - 410
08062500 TRINITY RIVER NEAR ROSSER, TEX.									
SiO_2	164	3.77	0.0110	11.2	3.56	0.66	2.67	24	200 - 1500
Ca	165	52.27	.0022	53.7	8.60	-.05	8.61	16	200 - 1500
Mg	165	1.09	.0064	5.35	1.89	.72	1.32	25	200 - 1500
Na	164	-55.12	.1964	76.6	43.2	.98	8.58	11	290 - 1500
K	51	-2.14	.0149	7.99	3.33	.93	1.25	16	200 - 1500
HCO_3	169	144	.0205	157	22.6	.18	22.2	14	200 - 1500
SO_4	167	-25.06	.1674	86.1	35.5	.97	8.24	10	200 - 1300
Cl	168	-31.08	.1319	56.4	28.1	.97	6.71	12	290 - 1400
DS	166	-25.29	.6412	403	140	.99	15.6	4	200 - 1500
HRD	169	132	.0350	156	22.5	.33	21.3	14	200 - 1500
NO_3	164	-25.60	.0717	22.5	17.1	.90	7.36	33	370 - 1500
PO_4	105	-5.93	.0164	5.27	4.11	.90	1.79	34	370 - 1500

Table 3. Results of regression analyses, $C_i = a_i + b_i K_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water years--Continued

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
08080500 DOUBLE MOUNTAIN FORK BRAZOS RIVER NEAR ASPERMONT, TEX.									
Ca	180	35.32	0.0894	466	234	0.93	86.9	19	900 - 9200
Mg	179	-15.98	.0187	74.1	49.6	.92	19.8	27	900 - 9200
Na	183	-87.58	.1427	596	355	.97	81.5	14	900 - 9200
K	44	4.45	.0009	9.02	2.82	.88	1.36	15	900 - 9200
HCO_3	195	99.18	.0009	103	22.3	.06	22.2	22	900 - 9200
SO_4	196	195	.2150	1210	549	.93	196	16	900 - 9200
Cl	197	-316	.2731	971	656	.99	81.1	8	1200 - 9200
DS	182	-119	.7381	3410	1810	.99	212	6	900 - 9200
HRD	195	46.99	.2960	1440	754	.94	267	19	900 - 9200
08087300 CLEAR FORK BRAZOS RIVER AT ELIASVILLE, TEX.									
Ca	175	19.99	0.0488	100	51.4	0.96	14.3	14	300 - 4850
Mg	175	-5.18	.0235	33.5	25.5	.93	9.39	28	300 - 4850
Na	173	-36.26	.1375	191	140	.99	16.8	9	300 - 4850
K	47	4.77	.0013	6.84	1.63	.78	1.03	15	300 - 4850
HCO_3	187	111	.0145	135	34.5	.42	31.3	23	300 - 4850
SO_4	186	-35.08	.1198	161	165	.72	114	71	300 - 4850
Cl	187	-74.29	.2689	366	278	.97	70.0	19	300 - 4850
DS	177	-53.75	.6031	947	619	.99	77.6	8	300 - 4850
HRD	187	30.17	.2161	384	227	.96	66.7	17	300 - 4850

Table 3. Results of regression analyses, $C_i = a + b_i K_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water year--Continued

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
				08111000 NAVASOTA RIVER NEAR BRYAN, TEX.					
Ca	206	15.58	0.0200	29.2	14.6	0.70	10.4	36	70 - 3400
Mg	206	3.95	.0057	7.82	3.83	.77	2.46	31	70 - 3400
Na	191	-12.84	.1474	71.4	44.1	.97	10.3	14	90 - 1450
Na	15	-45.31	.1879	349	129	.98	22.3	6	1451 - 3400
K	50	3.53	.0010	4.09	.64	.44	.58	14	70 - 3400
HCO_3	226	50.13	.0157	61.0	26.1	.31	24.8	41	70 - 3400
SO_4	226	30.63	.0102	37.7	18.6	.28	17.9	47	70 - 3400
Cl	208	-34.45	.2669	118	80.4	.98	16.2	14	130 - 1450
Cl	18	-81.02	.3259	594	204	.99	28.4	5	1451 - 3400
DS	224	8.90	.5241	374	276	.99+	18.9	5	70 - 3400
HRD	226	2.21	-.1115	1.97	.22	.41	.20	10	70 - 3400
				08114000 BRAZOS RIVER AT RICHMOND, TEX.					
Ca	148	22.19	0.0549	57.2	12.2	0.91	5.06	9	240 - 1050
Ca	34	46.71	.0304	86.3	7.92	.73	5.41	6	1051 - 1900
Mg	182	1.34	.0128	11.1	4.49	.94	1.58	14	240 - 1900
Na	149	-27.30	.1351	58.6	28.1	.98	5.54	9	240 - 1050
Na	34	-46.85	.1574	158	30.8	.98	5.79	4	1051 - 1900
K	35	3.15	.0011	3.91	.59	.44	.53	14	240 - 1900
HCO_3	189	123	.0435	156	30.5	.47	27.0	17	240 - 1900
SO_4	189	-18.03	.1265	77.3	42.2	.98	7.56	10	240 - 1900
Cl	154	-47.10	.2063	83.0	43.3	.98	8.06	10	240 - 1050
Cl	35	-90.06	.2513	236	49.6	.98	10.4	4	1051 - 1900
DS	184	-10.81	.5882	434	195	.99+	15.6	4	240 - 1900
HRD	189	72.77	.1688	200	5.77	.96	16.5	8	240 - 1900

Table 3. Results of regression analyses, $C_i = a_i + b_iK_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water years--Continued

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
08147000 COLORADO RIVER NEAR SAN SABA, TEX.									
Ca	162	28.30	0.0433	63.0	20.5	0.93	7.69	12	250 - 4200
Mg	162	3.99	.0219	21.6	11.8	.81	6.84	32	250 - 4200
Na	162	-37.45	.1326	68.9	59.4	.98	11.8	17	290 - 4200
K	41	3.04	.0015	4.14	.89	.54	.75	18	250 - 4200
HCO_3	174	194	.0068	199	46.1	-.03	46.1	23	250 - 4200
SO_4	170	-32.93	.1200	65.4	60.4	.91	24.9	38	280 - 4200
Cl	174	-81.97	.2490	126	119	.99	18.1	14	330 - 4200
DS	164	-14.68	.5780	460	270	.99+	24.9	5	250 - 4200
HRD	174	95.33	.1847	249	95.1	.92	37.5	15	250 - 4200
08164500 NAVIDAD RIVER NEAR GANADO, TEX.									
Ca	212	1.74	0.0934	43.6	21.7	.87	10.8	25	100 - 1050
Mg	212	.40	.1310	6.27	3.70	.71	2.60	41	100 - 1050
Na	156	-3.41	.0942	29.6	14.5	.91	6.10	21	100 - 600
Na	61	-71.17	.1944	65.5	18.3	.82	10.4	16	601 - 1050
K	67	3.02	.0013	3.51	.95	.26	.92	26	100 - 1050
HCO_3	218	3.64	.3448	157	72.6	.96	20.5	13	100 - 1050
SO_4	222	5.42	.0209	14.8	5.74	.73	3.92	26	100 - 1050
Cl	160	-9.01	.1377	39.3	20.5	.94	7.08	18	100 - 600
Cl	62	-76.02	.2374	90.5	21.0	.88	10.0	11	601 - 1050
DS	216	-2.14	.5831	258	118	.99+	10.2	4	100 - 1050
HRD	218	5.48	.2880	134	61.5	.95	20.1	15	100 - 1050

Table 3. Results of regression analyses, $C_i = a_i + b_iK_{sc}$, for selected chemical constituents for 12 Texas stations, 1962-66 water years--Continued

Variable (i)	No. of paired values	Intercept (a_i)	Regression coefficient (b_i)	Mean C_i	Standard deviation C_i	Correlation coefficient (r)	Std. error estimate (SE_e)	SE_e as percent of mean	Range in K_{sc}
08176500 GUADALUPE RIVER AT VICTORIA, TEX.									
Ca	133	11.00	0.0883	54.6	10.8	0.83	6.04	11	200 - 725
Mg	132	-6.05	.0400	13.7	4.52	.90	2.00	15	200 - 725
Na	134	-6.56	.0716	28.7	8.98	.81	5.31	19	200 - 725
K	33	5.62	.0054	3.01	.86	.68	.63	21	200 - 725
HCO_3	134	16.85	.3843	206	42.9	.91	18.2	9	200 - 725
SO_4	134	-.31	.0581	28.4	6.98	.83	3.90	14	200 - 725
Cl	90	-13.74	.1046	33.1	10.5	.87	5.19	16	200 - 550
Cl	44	-67.79	.1993	49.8	9.55	.69	6.95	14	551 - 725
DS	133	-6.26	.5923	286	61.1	.99	10.4	4	200 - 725
HRD	134	2.69	.3842	192	41.0	.95	12.9	7	200 - 725
08188500 SAN ANTONIO RIVER AT GOLIAD, TEX.									
Ca	169	14.53	0.0780	77.2	20.6	.96	6.03	8	200 - 1300
Mg	169	-2.65	.0228	15.7	6.03	.96	1.75	11	200 - 1300
Na	171	-15.15	.1060	69.4	28.4	.96	8.13	12	200 - 1300
K	42	6.37	.0001	6.30	1.24	-.16	1.26	20	200 - 1300
HCO_3	186	51.36	.2282	229	63.3	.95	19.6	9	200 - 1300
SO_4	185	-12.31	.1152	77.1	31.3	.97	7.30	9	200 - 1300
Cl	186	-27.75	.1457	85.4	39.8	.97	10.3	12	200 - 1300
DS	170	-9.31	.6109	480	159	.98	32.1	7	200 - 1300
HRD	186	16.47	.2978	248	80.6	.98	17.8	7	200 - 1300

Although SiO_2 (silica) is not appreciably ionized and does not directly affect the specific conductance, it is possible to have a significantly correlated C_{SiO_2}-K_{sc} relationship; as shown on figure 4a for Trinity River at Rosser, Texas. This relationship may exist where most of the dissolved constituents, including silica, are from one source, such as a reservoir or ground water discharge and concentrations tend to vary proportionately. Providing no changes which would significantly alter the C_{SiO_2}-K_{sc} relationship take place within a basin, a regression equation that accounts for a major portion of the variation in the dependent variable may be used as a predictive tool over the range in values experienced during the calibration period. The C_{SiO_2}-K_{sc} relations for most of the stations were poor, as exemplified by the graph for Guadalupe River at Victoria (fig. 4b). However, the basic statistics and plots do provide information on observed range and variation in concentrations experienced during the calibration period.

NO_3 (nitrate) data and limited PO_4 (phosphate) data generally show little relation to specific conductance, and range in concentrations are generally small for both variables (table 2). The one exception was for the Trinity River near Rosser. The quality of water at this station is greatly affected by municipal-waste discharge of the Dallas-Fort Worth metropolitan area. The significantly correlated C_{NO_3}-K_{sc} and C_{PO_4}-K_{sc} relationships (figs. 5a and 5b) exist because: (1) Streamflow of the Trinity River Basin above the Rosser station is highly regulated by water-supply reservoirs; (2) a large portion of the dissolved constituents, including NO_3 and PO_4, in water at the station are from municipal wastes; and (3) ranges in constituent concentrations and specific conductance result from dilution of fairly constant wastes discharges by variable runoff.

With the regression equation developed in this study, NO_3 and PO_4 concentrations can be calculated from specific conductance with a standard error of estimate expressed as a percentage of the mean of 33 and 34 percent, respectively, for the Trinity River at Rosser (table 3). However, because these nutrients are important factors in water use and pollution control, more accurate determinations of these constituents may be required.

Limited fluoride observations in the data set generally show only minor variations in concentrations and no relation to specific conductance (fig. 6a). As shown in the basic statistics (table 2), the maximum range in fluoride concentration of 0.2 to 2.3 mg/l occurred at Trinity River near Rosser, with the higher concentrations probably resulting from waste inflows.

No relation of pH to specific conductance is shown at any of the stations (fig. 6b), and none would be expected in any Texas streams. Adequate pH-K_{sc} relationships probably do exist in some U.S. streams receiving high alkaline or acidic industrial wastes or acid mine drainage.

Although C_i-K_{sc} relationships for SiO_2, NO_3, PO_4, F, and pH probably are poor for most surface-waters, the range in concentrations of these variables is generally limited in natural waters and where these ranges in concentrations have been determined by historical composite analyses, a reduced program to periodic analyses should serve most information needs. If one of these variables is likely to occur in concentrations that affect water use or exceed health or water-quality standards, analyses of discrete samples probably would be required to provide data for surveillance, control, or abatement procedures.

Examples of highly-correlated C_{DS}-K_{sc} and C_{Cl}-K_{sc} relationships for 1962-66 water-year data are shown on figures 7a, 7b, 8a, and 8b. The correlation coefficients (r), presented in table 3, provide an index which measures the closeness of fit of observed points to the estimated regression line. Snedecor (1946, p. 148-155) discusses methodology that can be used to judge whether or not a computed r is significantly different from zero. The following table presents the value of r which must be equalled or exceeded at the 1 percent level of significance before the computed r can be considered to be significantly different from zero (Snedecor, 1946).

Figures 7a, 7b, 8a, and 8b (captions on next page) belong near here.

Degrees of freedom (number of paired observations -2)	Value which computed r must exceed before null hypothesis, $\rho = o$ is rejected
10	0.708
30	.449
50	.354
100	.254
150	.208
200	.181

The square of the correlation coefficient (coefficient of determination) is useful in explaining what percentage of the total variation is due to or accounted for by the regression.

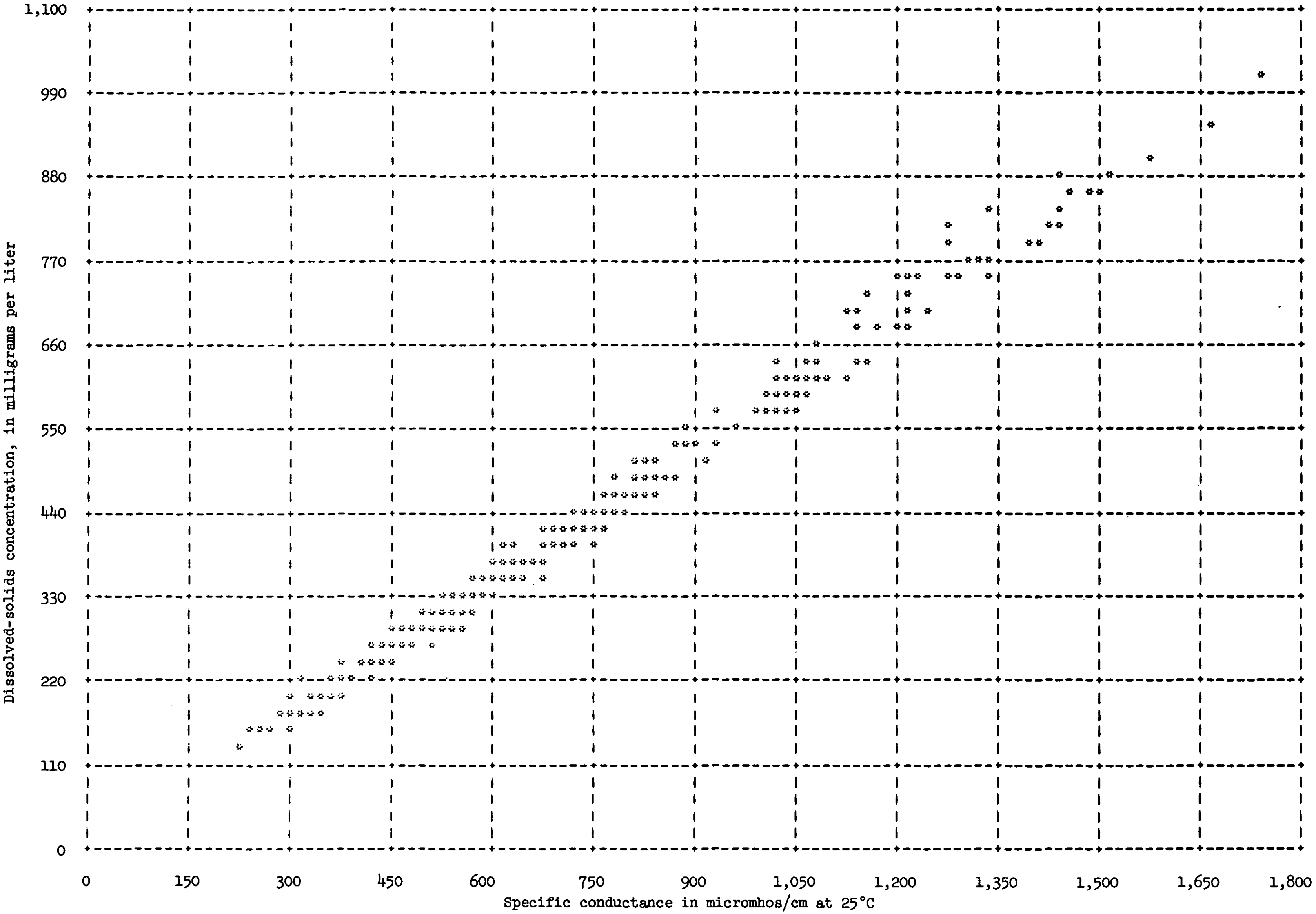

Figure 7a.--Dissolved solids versus specific conductance for station 08114000, Brazos River at Richmond, Tex.

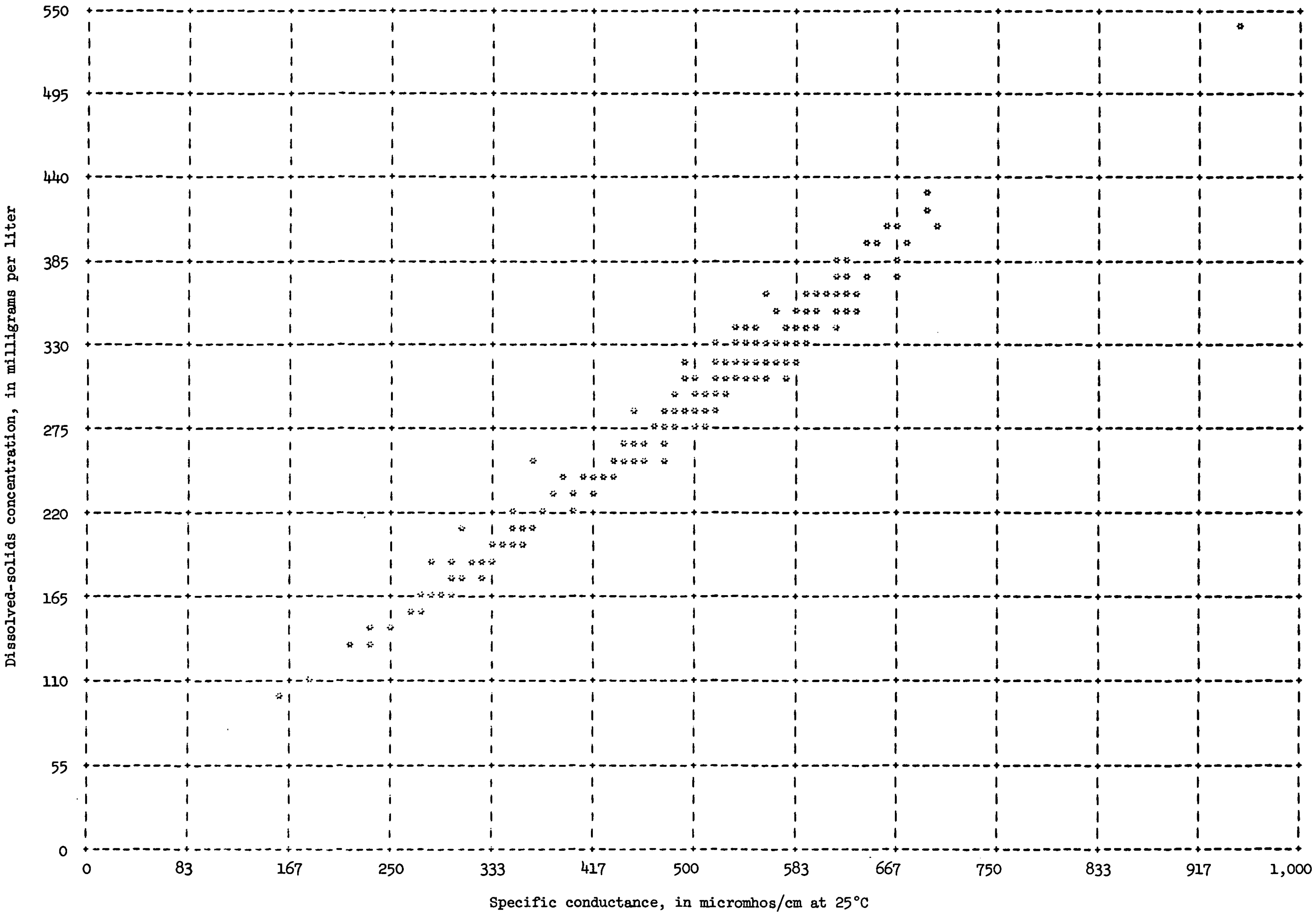

Figure 7b.--Dissolved solids versus specific conductance for station 08176500, Guadalupe River at Victoria, Tex.

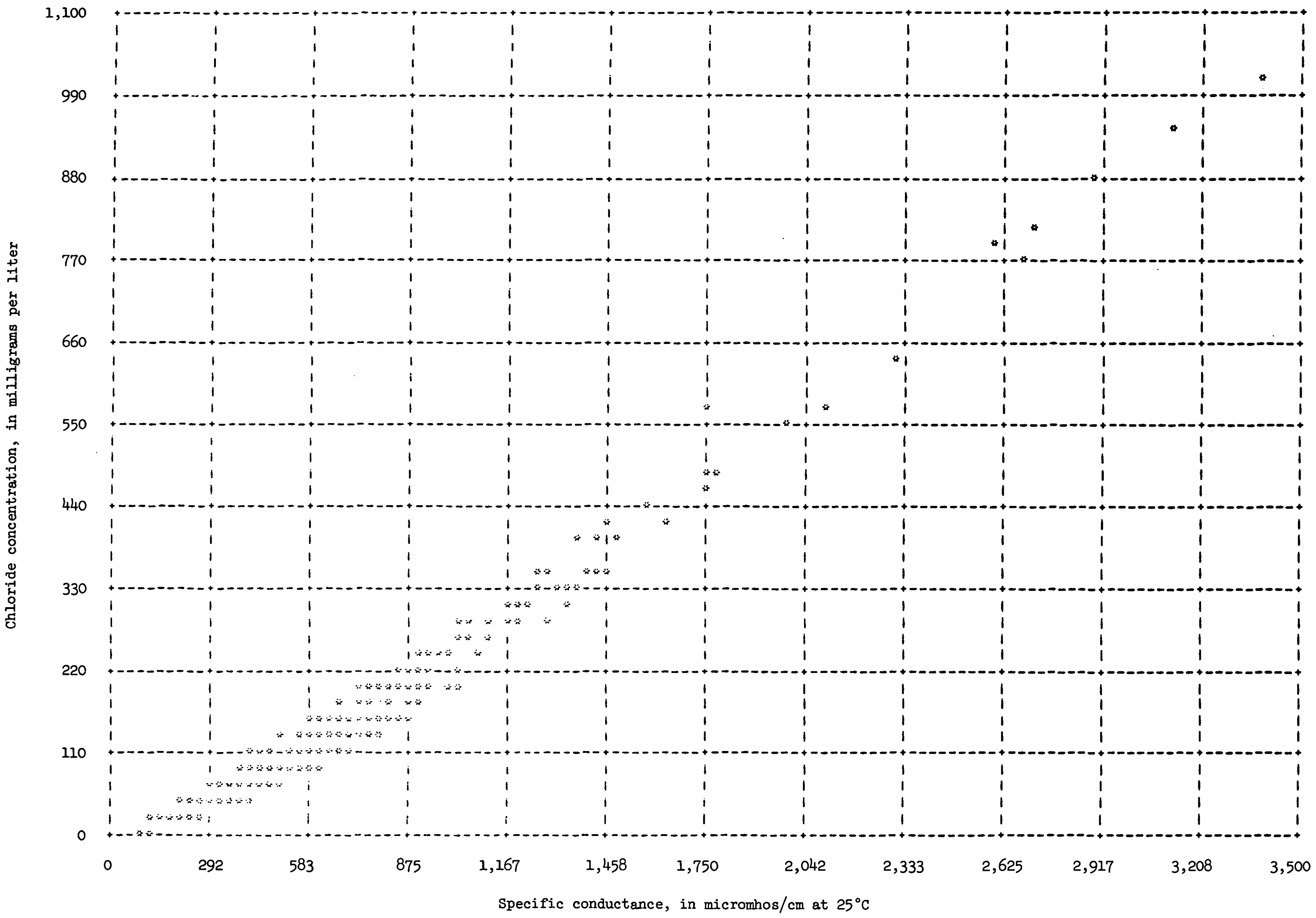

Figure 8a.--Chloride versus specific conductance for station 08111000, Navasota River near Bryan, Tex.

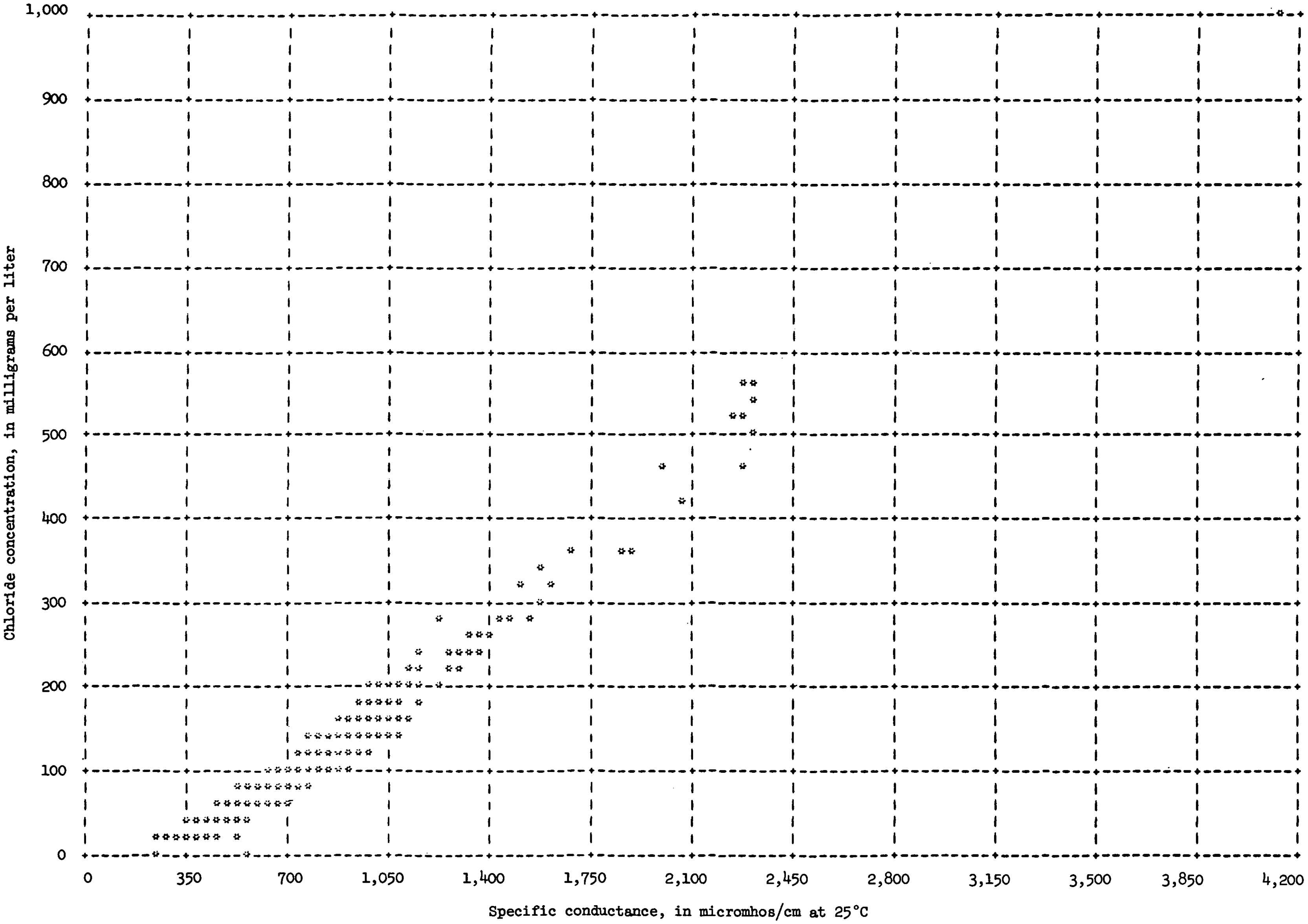

Figure 8b.--Chloride versus specific conductance for station 08147000, Colorado River near San Saba, Tex.

Regression equations developed from the 1962-66 data sets for Ca (calcium), Mg (magnesium), Na (sodium), K (potassium), HCO_3 (bicarbonate), SO_4 (sulfate), Cl (chloride), and dissolved solids (table 3) were used in conjunction with daily water-discharge and specific-conductance values to simulate chemical-quality data for 169 station years (table 1). The simulated records include time- and discharge-weighted weekly, monthly, and annual summaries of concentrations and loads.

Annual discharge-weighted average concentrations were available for all station years in the historical data set, and these values were compared to the corresponding simulated values. All records outside the 1962-66 calibration period serve as test data for the regression. As an example, residuals obtained by substracting simulated from actual discharge-weighted concentrations (mg/l) for the Brazos River at Richmond are plotted on figure 9. Actual discharge-weighted concentrations of dissolved solids versus time are also plotted on figure 9 to show extremes and yearly variations in total dissolved constituents. Actual and simulated annual discharge-weighted concentrations for the 1946-69 water-year period for this station are shown in table 4.

Figure 9 (caption on next page) belongs near here.

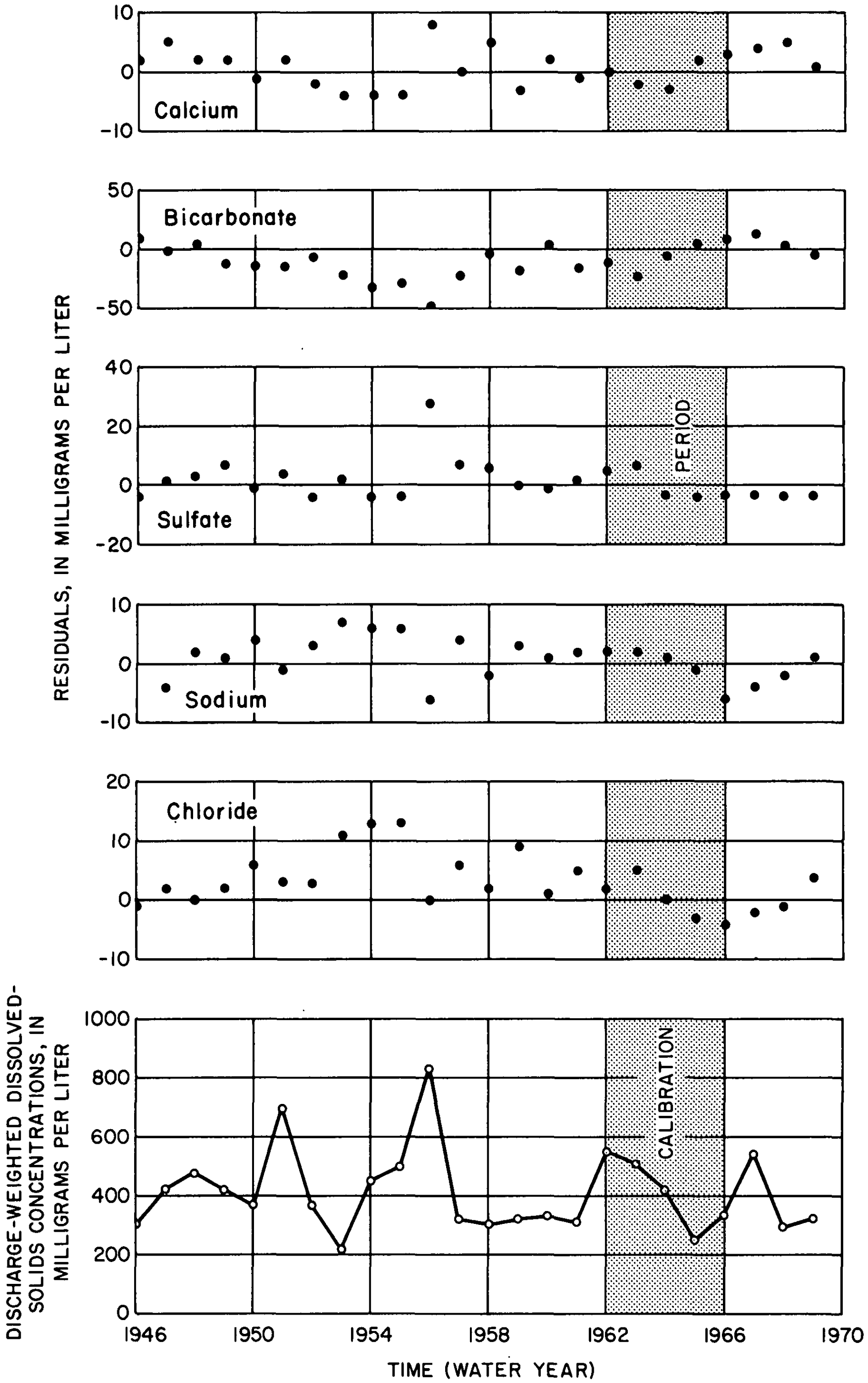

FIGURE 9.–Residuals in milligrams per liter (actual-simulated) for selected chemical constituents for the Brazos River at Richmond, Texas

TABLE 4.--Actual and simulated annual discharge-weighted concentrations for the Brazos River at Richmond, Texas, 1946-69 water years

(Results in milligrams per liter)

Constituents	Date source	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969
Ca	Actual	51	63	65	59	53	80	51	36	55	60	95	50	54	49	54	49	71	66	58	49	58	77	56	54
	Simulated	49	58	63	57	54	78	53	40	59	64	87	50	49	52	52	50	71	68	61	47	55	73	51	53
Mg	Actual	8.6	11	11	10	8.1	16	8.8	5.7	9.1	8.9	14	6.9	7.7	8.0	9.0	8.0	12	12	11	6.9	8.4	13	6.9	7.9
	Simulated	7.6	10	11	10	9.1	16	9.1	5.5	11	12	19	7.9	7.6	8.3	8.3	7.9	13	13	11	7.1	9.0	14	8.0	8.6
Na	Actual	37	63	82	70	60	139	60	23	83	95	166	46	37	49	48	44	106	97	77	32	48	101	41	51
	Simulated	39	67	80	69	56	140	57	16	77	89	172	42	39	46	47	42	104	95	76	33	54	105	43	50
K	Actual	--	--	--	--	--	2.4	2.8	3.8	4.1	4.9	5.8	--	3.8	4.5	--	--	--	--	--	--	--	4.4	--	--
	Simulated	3.7	3.9	4.0	3.9	3.8	4.4	3.8	3.5	4.0	4.1	4.7	3.7	3.7	3.8	3.8	3.7	4.2	4.1	4.0	3.6	3.8	4.2	3.7	3.8
HCO_3	Actual	155	152	162	141	136	160	143	115	124	132	136	124	142	130	151	132	153	140	151	149	159	180	150	145
	Simulated	145	153	157	153	150	174	150	137	156	160	184	146	145	147	147	146	164	162	156	143	149	165	146	148
SO_4	Actual	39	70	84	76	58	134	54	25	72	83	185	54	50	51	50	49	106	100	74	35	54	100	45	51
	Simulated	43	69	81	69	59	130	58	23	76	87	157	47	44	51	51	47	101	93	77	39	57	103	48	54
Cl	Actual	53	100	118	103	87	214	85	31	127	145	260	65	57	74	67	64	156	145	111	43	72	153	60	75
	Simulated	54	98	118	101	81	211	82	20	114	132	260	59	55	65	66	59	154	140	111	46	76	155	61	71
DS	Actual	299	425	479	423	368	696	370	215	453	498	834	317	303	323	331	312	551	513	419	251	333	545	294	323
	Simulated	275	392	448	395	346	678	344	180	426	479	804	290	279	308	311	290	543	506	429	254	340	553	296	323

Residuals of calcium concentrations for the Brazos River at Richmond appear to be randomly scattered around the line of zero residual, indicating that the C_{Ca}-K_{sc} relationship for the 1962-66 period is valid over the 24 years of historical record. The difference in simulated calcium values was less than ± 10 percent of the corresponding actual values for all years.

Bicarbonate residuals for this station were frequently negative, with simulated annual concentrations exceeding the actual in 14 of the 19 years in the test period (1946-61, 1967-69). Residuals (in percentage of actual) were usually less than 20 percent, except for 1956 when the HCO_3 residual was -35 percent (actual 136 mg/l, simulated 184 mg/l). The discharge-weighted dissolved-solids concentration for 1956 was 834 mg/l, maximum for the period of record. The C_{HCO_3}-K_{sc} relationships were poor for 7 of the 12 stations, because maximum bicarbonate concentrations are more limited by saturation than other ions are, resulting in low C_{HCO_3}-K_{sc} correlations (see Steele, 1971).

Specific conductance may increase above a certain level with no increase, and in some waters a decrease, in HCO_3 concentration. Regression equations for C_{HCO_3}-K_{sc} can probably be developed for many surface waters by segmenting the nonlinear rating curves into the approximate linear portions and developing regression equations for ranges in K_{sc} within each of the line segments. For some surface waters, the maximum HCO_3 concentration may be arbitrarily set as a constant when specific conductance values exceed the observed linear range for C_{HCO_3}-K_{sc}.

Sulfate residuals were small and randomly scattered about the zero residual line. Difference in actual versus simulated values for sulfate was usually less than ± 10 percent for the Brazos River station.

Although residuals for Na and Cl concentrations for Brazos River at Richmond were generally small, they were positive for most years before 1964. The change from positive to negative residuals in the mid-sixties may be due to a change in dissolved-constituent composition, but most likely results from random errors in simulation. The highest Na residual of +7 mg/l (30 percent) and a high Cl residual of +11 mg/l (35 percent) occurred in 1953 when the minimum annual weighted-average dissolved-solids concentration for the period of record occurred. Na and Cl residuals (in percentage of actual) were usually much less than ± 10 percent for all other station years. Regression equations for C_{Na}- and C_{Cl}-K_{sc} developed for the upper and lower segments of the slightly nonlinear plots probably would improve the C_i-K_{sc} relationships for Na and Cl concentrations for this station.

Actual and simulated annual discharge-weighted concentrations for the Guadalupe River at Victoria, Texas, 1946-69 water years are shown in table 5. The plot of residuals for selected constituents for the Guadalupe River station (fig. 10) showed trends over time, indicating some shifting in the C_i-K_{sc} regression relationships before the calibration period. Residuals (actual minus simulated) for Ca and HCO_3 changed from negative to positive and Na and Cl residuals changed from positive to negative about the 1957 water year. Rawson (1968, p. 11) discussed the change in chemical composition, the decline in Na and Cl concentrations, and the resulting shift in Ca-HCO_3 and Na-Cl relationships to specific conductance.

Figure 10 (caption on next page) belongs near here.

Since the mid-fifties, the volume of oil-field brines reaching the streams in the upper Guadalupe Basin has been reduced, with all or most of these brines now being injected in deep wells. As shown by the residual plots in figure 9, systematic errors are caused by using the regression equations developed from the 1962-66 calibration period for simulating records during the 1946-57 water year period for this station. If regression equations are to be used to compute chemical concentrations and loads for current data-collection activities, sufficient laboratory analysis of samples should be included in the continuing data-collection program to provide periodic checks of the C_i-K_{sc} relationships. Revised C_i-K_{sc} regression equations should be developed when any significant shifts are detected for any of the constituents.

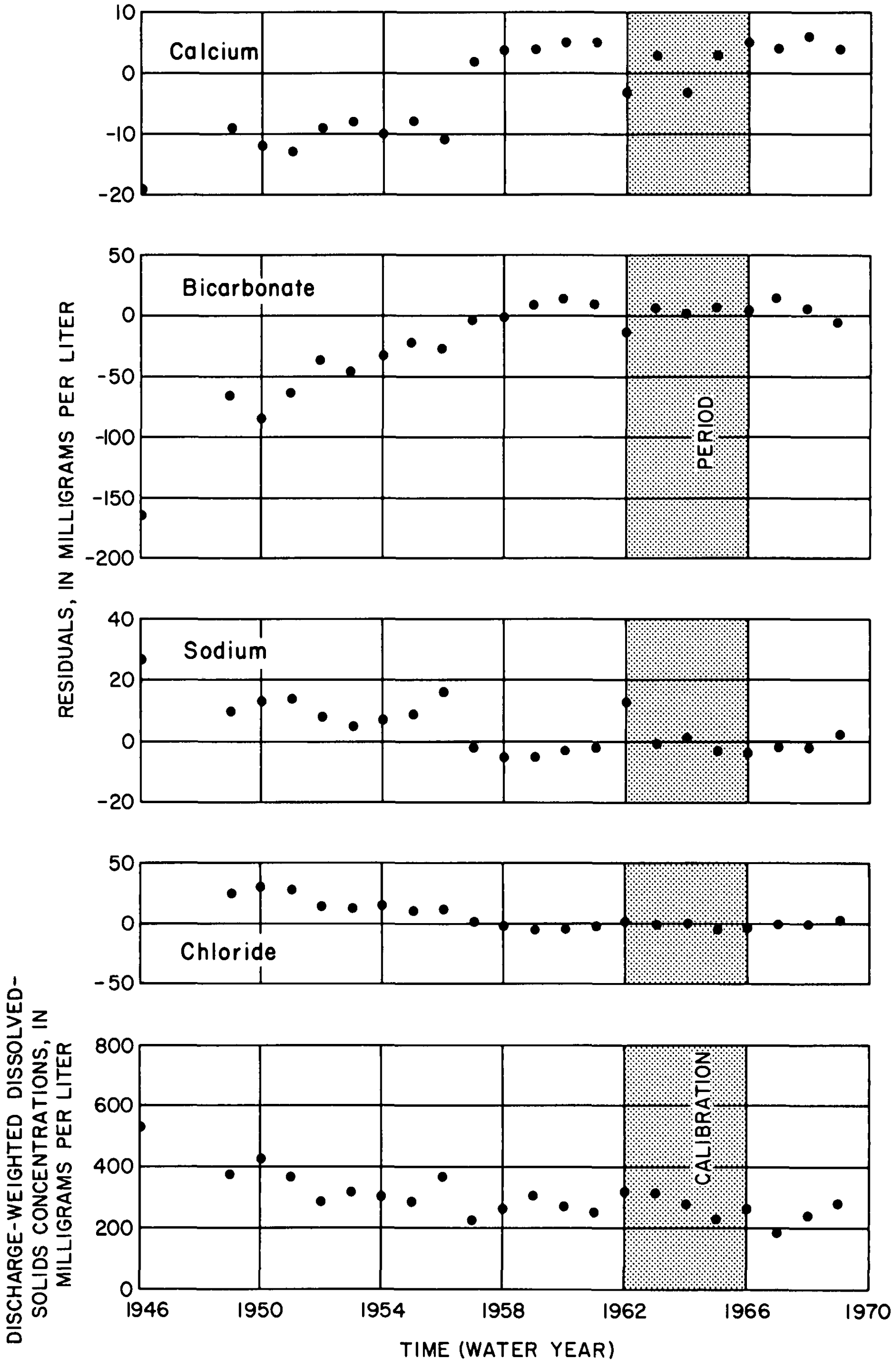

FIGURE 10.—Residuals in milligrams per liter (actual-simulated) for selected chemical constituents for the Guadalupe River at Victoria, Texas

TABLE 5.--Actual and simulated annual discharge-weighted concentrations for the Guadalupe River at Victoria, Texas, 1946-69 water years

(Results in milligrams per liter)

Constituents	Data source	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969
SiO_2	Actual	--	--	--	14	15	16	17	17	19	18	16	13	14	15	16	15	17	15	13	11	11	9.5	11	12
	Simulated	18	18	22	15	16	15	14	14	14	14	15	12	13	14	14	13	14	14	14	13	14	12	13	14
Ca	Actual	69	--	--	57	60	53	45	51	46	46	56	45	53	60	58	53	55	61	51	51	57	44	54	57
	Simulated	88	85	118	66	72	66	54	59	56	54	67	43	49	56	53	48	58	58	54	48	52	40	48	53
Mg	Actual	18	--	--	15	17	17	12	14	14	12	16	7.3	11	14	13	11	16	15	14	10	12	7.6	9.8	11
	Simulated	29	27	43	19	22	19	13	15	14	14	20	8.6	11	14	13	11	15	15	13	10	13	7.2	11	13
Na	Actual	83	--	--	48	56	52	36	37	37	38	55	18	20	25	25	22	35	31	29	20	23	15	22	29
	Simulated	56	53	80	38	43	38	28	32	30	29	39	20	25	30	28	24	32	32	28	23	27	17	24	27
K	Actual	--	--	--	--	--	1.0	2.8	3.7	3.4	3.6	3.9	4.5	3.3	2.8	--	--	--	--	--	--	3.0	3.2	--	--
	Simulated	10	10	12	9.0	9.4	9.0	8.2	8.5	8.4	8.3	9.1	7.6	8.0	8.4	8.2	7.9	8.5	8.5	8.2	7.9	8.2	7.4	7.9	8.2
HCO_3	Actual	191	--	--	190	199	195	166	179	179	184	235	153	183	219	215	188	210	230	203	183	202	158	185	193
	Simulated	354	338	484	255	283	258	202	224	212	206	262	157	184	211	201	178	223	223	202	176	197	144	179	199
SO_4	Actual	39	--	--	28	32	30	24	29	27	27	30	21	27	28	27	24	34	31	26	24	27	15	25	31
	Simulated	51	48	70	36	40	36	28	31	29	28	37	21	25	29	28	24	31	31	28	24	27	19	24	27
Cl	Actual	160	--	--	86	104	89	56	61	58	51	72	26	31	35	33	29	47	42	37	26	33	20	30	40
	Simulated	109	101	176	61	73	61	42	48	43	40	60	25	33	40	37	32	45	43	37	30	36	21	31	38
DS	Actual	532	--	--	380	425	371	291	319	304	293	368	227	264	303	288	258	321	316	281	236	266	191	246	284
	Simulated	513	488	714	361	405	366	279	312	295	285	372	210	252	293	278	243	312	311	279	239	272	190	244	275

The comparison of simulated data to historical records, computed from composite samples, tests the predictive capability of the C_i-K_{sc} regression equations and indicates the levels of accuracy that can be expected if regression equations and daily specific-conductance values are used conjunctively to produce current information on chemical quality. This comparison also points out changes in the relative abundances of ions if and when changes in composition occur. The differences between simulated and actual constituent values are influenced by random errors, and may be influenced by compositional changes. However, the comparisons also appear to be partly biased by differences between the composite and daily specific-conductance records.

Figure 11 shows a plot of annual mean discharge-weighted specific conductance values from composites versus annual mean discharge-weighted specific conductance values from daily samples for the Neches River at Evadale. The relationship is very good, but most of the data points fall above the line of equivalence (intercept = 0, slope = 1.00), showing annual averages from composites to be consistently, but only slightly higher than those from daily values.

Figure 11 (caption on next page) belongs near here.

The higher discharge-weighted specific-conductance values for periods of similar specific-conductance results from use of equal volumes of the daily samples instead of volumes proportional to discharge. Compositing by equal volume results in a time-weighted sample for the composite period, which is likely to be slightly higher than a discharge-weighted composite for the same period.

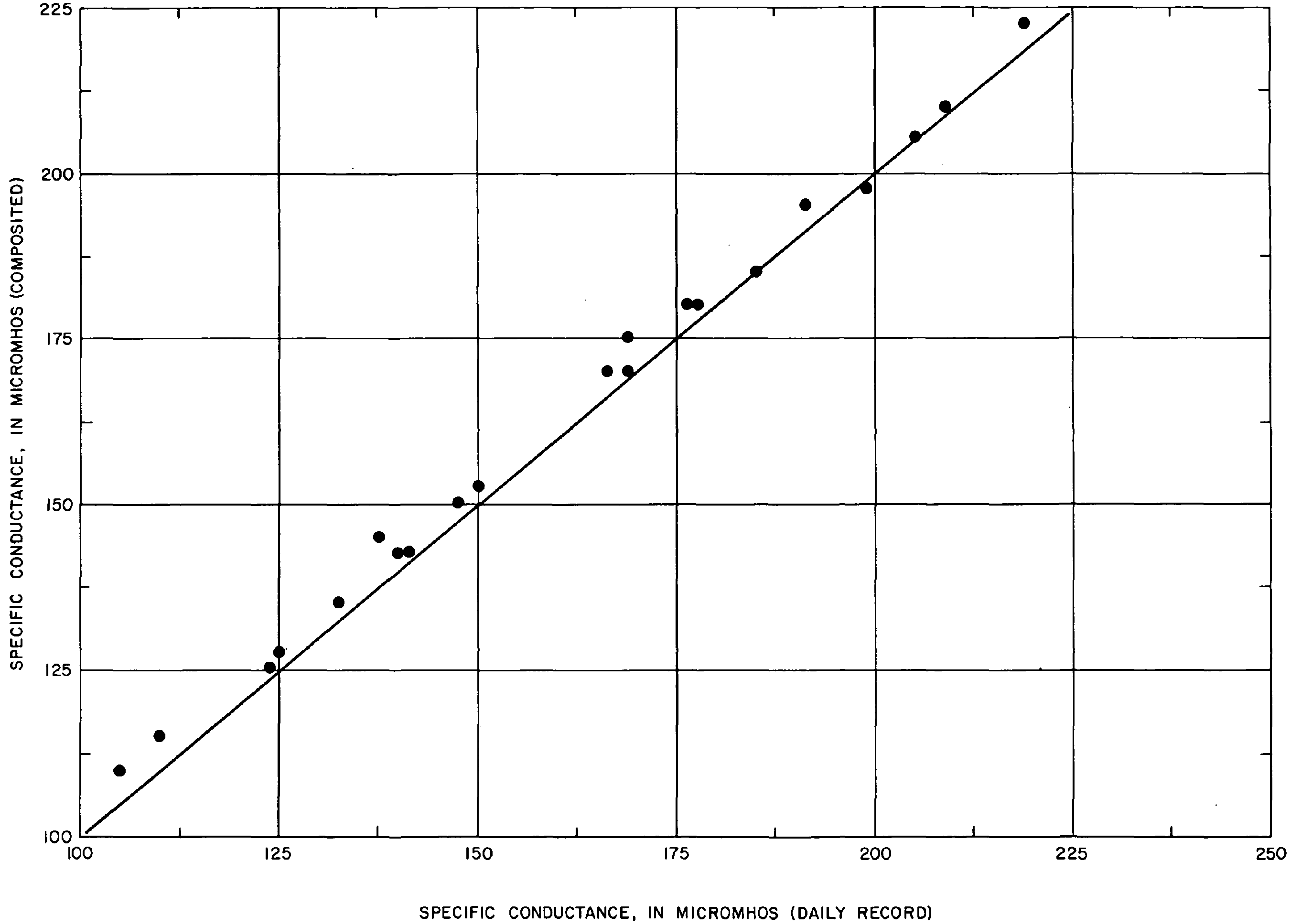

FIGURE 11.-Annual discharge-weighted specific conductance values from composite samples versus values from daily samples, Neches River at Evadale

Annual mean discharge-weighted specific conductance values from composited samples are actually discharge-weighted values for a group of time weighted composites. Of course, the same thing is done when one daily value is used to represent the discharge for that day--only the time-weighting period is shortened. The purpose of this discussion is not to criticize past or present data-collection activities, but to point out one source of bias not associated with the regression equations that may account for some of the differences between actual and simulated values reported in this study.

The only significant change in the relative abundance of ions observed in the analysis of streamflow chemical-quality data for the 12 stations was for the Guadalupe River at Victoria (fig. 10). Figure 12 shows actual and simulated annual mean discharge-weighted concentrations of calcium, chloride, and dissolved solids for the Neches River at Evadale, Texas. Actual and simulated values for calcium and chloride agree very well, and the plots show no time trends over the 22-year period. However, the actual dissolved-solids concentrations are greater than the simulated values from 1948 through 1955 and much greater during 1948-50.

Figure 12 (caption on next page) belongs near here.

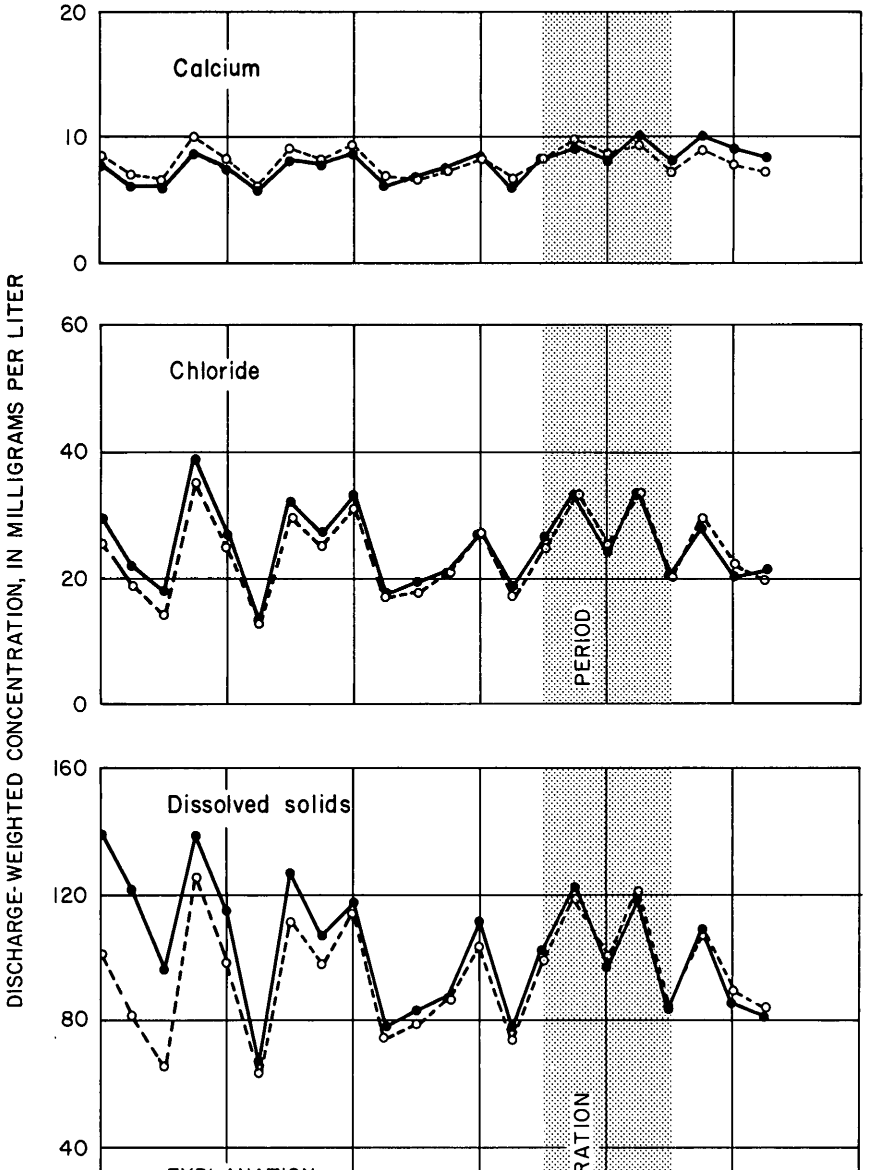

FIGURE 12.- Actual and simulated discharge-weighted concentrations of calcium, chloride, and dissolved solids for Neches River at Evadale, Texas

The high positive residuals (actual minus simulated concentrations) indicated that the C_{DS}-K_{sc} regression equation developed from the 1962-66 calibration period simulates a record for the 1948-55 test period with errors as large as 30 percent, suggesting a decrease in dissolved-solids concentrations relative to the level of specific conductance over time. However, the consistently positive residuals during the 1948-55 test period result to a large extent from a change in analytical procedures for determining dissolved-solids concentrations.

The dissolved-solids concentrations used in developing the regression equations were all calculated sums of determined constituents; whereas, the majority of dissolved-solids concentrations reported from 1948-55 were determined by residue on evaporation. The residue values at this particular sampling location include dissolved organic materials and probably average 10-20 percent higher than the sum of determined constituents. The differences in annual specific conductance values (fig. 11) also would account for part of the discrepancy shown in figure 12. In the analysis of historical data and in the application of regression equations for simulating chemical quality, problems of this nature must be taken into account in testing the adequacy of the regression procedure.

SUMMARY AND CONCLUSIONS

The water-quality records for the 12 stations evaluated in this study are considered to be representative of the variability in location and in the level of salinity of water of Texas streams. Concentration-discharge plots generally show poor relationships for all of the selected stations and should be an indication of the limitations for prediction of solute concentrations from water discharge in Texas streams. On the other hand, concentration-specific conductance plots and subsequent regression equations developed for each station using data from the 1962-66 water years and testing with available data outside this period indicate that specific conductance can be used as an index variable for estimating selected solute concentrations in Texas streams and that this procedure, with few exceptions, can be used as an alternative to composite analyses for calculation of solute concentrations and loads.

Results of regression analyses and comparisons of simulated versus actual data indicate that specific conductance records can be used in conjunction with C_i-K_{sc} regression equations (table 3) to calculate annual dissolved-solids concentrations and loads within 10 percent of results from laboratory values and annual Ca, Mg, Na, Cl, and SO_4 concentrations and loads usually within less than 20 percent. By developing regression equations for segments of the C_i-K_{sc} relationships for each station, accuracy of estimation can be improved for several of the cases studies. Estimates of HCO_3 concentrations can be improved by using two or more regression equations over the observed K_{sc} range or by using the maximum HCO_3 value as a constant for all K_{sc} values above a determined level as indicated by the historical data.

As might be expected, the C_i-K_{sc} relationships were generally poor for SiO_2, F, NO_3, PO_4, and pH; but the observed range in concentrations of these constituents were usually very limited, and variability in concentration has been fairly well defined by the historical data. If these constituents are likely to be present in concentrations that exceed water-quality standards or limit water use, analysis of individual samples at a determined sampling frequency should be continued in the data-collection program to monitor the problem or potential problem. Otherwise, data collection for these constituents should be reduced.

The use of specific conductance as an index variable in conjunction with concentration-specific conductance regression equations is a flexible system that can be applied with sufficient accuracy to satisfy most anticipated needs for data. For water management, daily specific-conductance determinations, or continuous specific-conductance records from monitors, accompanied by periodic analyses of the inorganic constituents to serve as continued checks on the regressions, would probably be required. For stations providing data for planning and design purposes, less frequent measurements of specific conductance may be sufficient along with the periodic check chemical analyses.

This report summarizes and discusses the results of several data-analysis procedures for historical water-quality records for 12 Texas stations. As of the 1971 water year, over 60 additional Texas stations, each having between six and 33 years of record, have data amenable for the type of analysis used in this report. If these records were analyzed using the procedures prescribed in this study, additional techniques, such as regionalization of chemical-quality conditions and an assessment of frequency-of-sampling alternatives, could be tested.

A change in station activities from composite chemical analyses to estimated values of solute concentrations and loads using simulative techniques should result in decreased costs and manpower requirements for this one facet of the water-quality data-collection programs. The resources made available by this reorientation may well be applied to other areas of water-quality programs currently constrained by lack of additional manpower and laboratory facilities. Net savings will depend both on information needs and specified accuracy criteria that are required in the overall water-quality program.

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