Relationships Between Ground-Water Silica, Total Dissolved Solids, and Specific Electrical Conductivity

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ABSTRACT

Specific electrical conductivity (SEC), total dissolved solids (TDS), and silica (SiO_2) are ground-water quality parameters routinely measured in a laboratory. Electrical conductivity measurements are made quickly and are less costly than TDS measurements. Once the relationship between the parameters is determined by regression analysis, TDS can be estimated quickly from the SEC and SiO_2 measurements. Water quality data from 25 city wells in Fresno, California, and historical ground-water quality data from the adjacent San Joaquin River/Kings River alluvial interfan (central San Joaquin Valley, California), the Kaweah River alluvial fan, and the Kern River alluvial fan (southern San Joaquin Valley) were used in this investigation. For the specific hydrologic areas studied, the model's TDS predictive ability is improved when SiO_2 is included with SEC as the independent variables.

INTRODUCTION

Specific electrical conductivity (SEC) measurements have been used to estimate total dissolved solids (TDS) concentrations in mountain streams (Singh and Kalra, 1975) and rivers (Lystrom *et al.,* 1978). The differences in SEC between single salt solutions within a wide range of concentrations has been described (U.S. Salinity Laboratory Staff, 1954). In dilute waters that contain moderate concentrations of SO_4^{2-}, HCO_3^-, and CO_3^{2-}, the specific conductance generally underestimates analytical concentrations (Tanji, 1969) because conductance is a measure of only those solutes that are dissociated (ionized).

Since natural ground waters are not single salt solutions or completely ionized salt solutions, the SEC will not relate singularly to TDS. Many ground waters contain $Si(OH)_4$ in the un-ionized form because the pH of the water is less than 9 and, therefore, is not included in the SEC measurement but is included in the TDS measurement. Thus, a regression model to predict TDS from SEC measurements can be in error because silica is not considered.

SEC values are useful as an indication of the dissolved solids or as a base for extrapolating other chemical data when only a partial chemical analysis is known (Hem, 1970). The SEC measurement procedure is simple, rapid, precise, and portable instruments are available for field analysis that produce valid data when used and maintained according to manufacturer's instructions.

TDS measurements are time-consuming. The procedure requires several days for evaporation and drying of a known volume of filtered water under constant and standard laboratory conditions (Standard Methods, 1975). The "total residue" is the sum of the "nonfilterable residue," the part of the total residue that the filter retains and the "filterable residue" or total dissolved solids (TDS), the part that passes through the filter. The terms "suspended" and "dissolved" solids have been used in the past for nonfilterable and filterable residue, respectively. Different drying temperatures give correspondingly different results because of residue weight changes caused by oxidation, loss of water of crystallization, volatilization of organic matter, mechanically occluded water, and gases from heat-induced chemical composition (Sokoloff, 1933; Howard, 1933). These variations can be minimized by the choice of the optimal drying temperature (Standard Methods, 1975).

Silicon (Si) in water is in the form of its oxide, silica (SiO_2), or its hydrated form, $Si(OH)_4$. Sixty percent of the earth's crust is composed of silicate minerals; therefore, silica constitutes the bulk of common rocks, soils, clays and sands (Nebergall *et al.*, 1963; Iler, 1955). Waters that drain from deposits high in silicate minerals,

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particularly feldspars, often contain up to 60 mg/l of SiO_2.

The rate at which SiO_2 goes into solution is related to the particle surface area over which the water passes. The mechanism of the dissolution of SiO_2 is one of simultaneous hydration and depolymerization.

$$(SiO_2)_n + 2n(H_2O) \overset{OH^-}{\underset{H^+}{=}} nSi(OH)_2$$

The reaction is catalyzed by bases and salts and retarded by acid salts. As the pH of the water increases above a pH of 9, the solubility of the hydrated form increases because of the formation of the silicate ion (Iler, 1955).

$$Si(OH)_4 + H_2O + OH^- = (H_2O)\ Si\ (OH)_5^-$$

Ground waters that contain high silica (> 45 mg SiO_2/l) are undesirable from the standpoint that "water spots" form on glass surfaces that cannot be removed by commonly used household glass cleaners.

The purpose of this paper is to show that TDS can be estimated with less error from SEC by accounting also for the presence of silica once the relationship between the three parameters has been defined for a given area.

STUDY AREAS

The published data on the silica content of ground waters (unconfined aquifers) in the far eastern fourth of the San Joaquin Valley in California showed some areas with more than 10 mg SiO_2/l. Four of the areas were considered for this investigation.

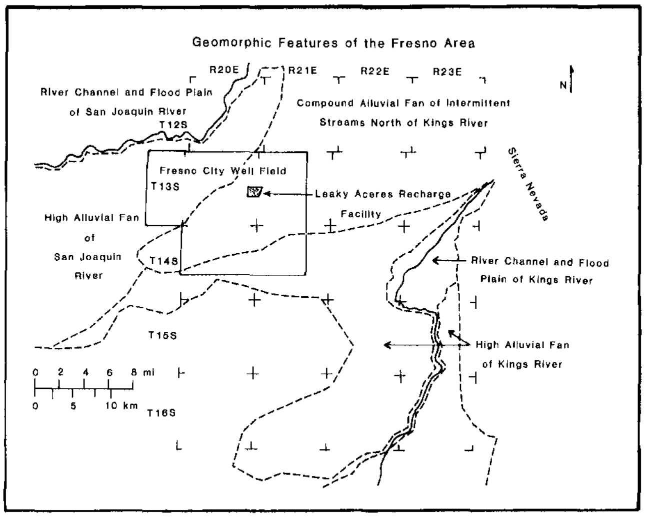

Fig. 1. Geomorphic features of the Fresno area.

The Fresno area, that portion of the San Joaquin/Kings River interfan (Page and LeBlanc, 1969) formed by coalescing sedimentary deposits from three sources: (a) the San Joaquin River's high and low alluvial fans, (b) the Kings River's high and low alluvial fans, and (c) an intermediary compound alluvial fan formed by four small ephemeral streams that drain a 344 km^2 (125 mi^2) watershed between the two major rivers (Figure 1). The San Joaquin and Kings Rivers drain a 128 km (80 mi) linear segment of the Sierra Nevada. They have watersheds of 4532 km^2 (1750 mi^2) and 4455 km^2 (1720 mi^2), respectively.

The Visalia (Figure 2) and Bakersfield (Figure 3) areas, with drainages of 1660 km^2 (640 mi^2) and 5900 km^2 (2280 mi^2), are defined as the alluvial fans of the Kaweah and Kern Rivers, respectively,

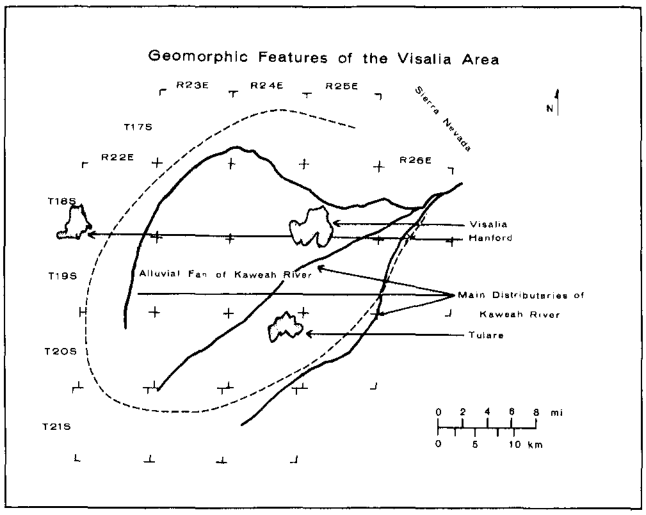

Fig. 2. Geomorphic features of the Visalia area.

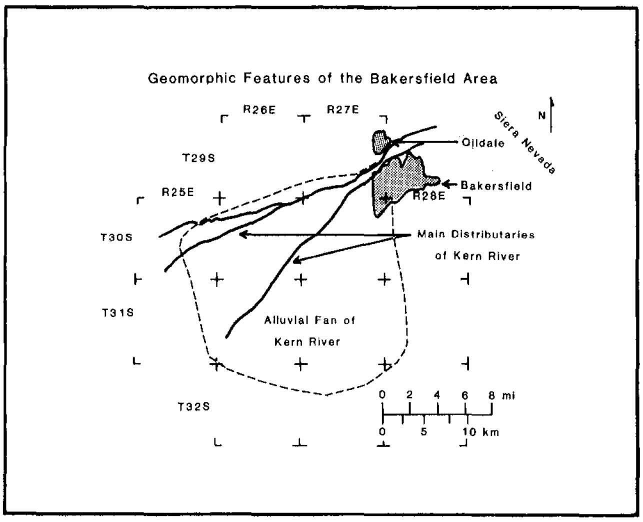

Fig. 3. Geomorphic features of the Bakersfield area.

and drain the southern 153 km (95 mi) linear segment of the Sierra Nevada.

Twenty-five Fresno City wells (Figure 1) were sampled in the Summer of 1977. They are located in the northwest portion of the Fresno City well field and pump from the unconfined aquifer of the intermediary compound alluvial fan. Also shown in Figure 1 is the Leaky Acres Ground-Water Recharge Facility (Nightingale and Bianchi, 1977) owned and operated by the City of Fresno.

METHODS

Ground-water samples were collected from 25 Fresno City wells. SEC was determined with a Beckman conductivity bridge using a pipette cell. The TDS analyses (103-105C) were run on two samples within each 25 mS/cm increment of the entire SEC range of 75 to 550 mS/cm using Standard Methods (1975). Silica was determined by the molybdosilicate method (Standard Methods, 1975).

After defining the Fresno, Visalia and Bakersfield areas on maps, the SEC, TDS, and SiO_2 data for these areas were collected from ground-water quality data lists from the USDA Water Management Research Laboratory, Fresno, California (Nightingale *et al.*, 1970a; Nightingale *et al.*, 1970b; Nightingale *et al.*, 1972; Nightingale and Bianchi, 1980) and the California State Department of Water Resources, Fresno, California (DWR Bulletins No. 66-60 through 66-62; DWR Bulletins No. 130-63 through 130-75). The regression equations for TDS as a function of SEC and as a function of SEC + SiO_2 were determined for each study area (Draper and Smith, 1966).

In order to study changes in SiO_2 concentration of percolating water under known conditions, surface and ground-water samples were taken at the Leaky Acres Recharge Facility. Ground-water samples were obtained from a tile line at a depth of 1.5 m (5 ft); a shallow 4.0 m (13 ft) well perforated in the last 30 cm (1 ft); and nine observation wells with sampling depths of 16.9 m (55.5 ft) to 20.6 m (67.7 ft) with a mean depth of 18.7 m (61.4 ft). The water samples were analyzed for TDS, SEC, and SiO_2 (Standard Methods, 1975).

RESULTS AND DISCUSSION

Table 1 presents the statistics for the study areas based on the number of observations (n) and years of data considered. Excluding the Fresno City wells, the lowest mean SEC, TDS, SiO_2 was in the Visalia area and the highest mean SEC, TDS, and SiO_2 was in the Fresno area. The highest values for SiO_2 were found in the Fresno City well-water samples.

Regression equations for TDS similar to those used to estimate TDS from SEC measurements for mountain streams (Singh and Kalra, 1975) and rivers (Lystrom *et al.*, 1978) are given in Table 2 for ground water in the four study areas. These simple linear equations are applicable to the ranges in SEC presented in Table 1. The coefficient of determination, r^2, shows the fraction of variability in TDS accounted for by SEC. Thus, for example, in the Fresno area, 98.2% of the variability in TDS is accounted for by SEC and 1.8% by some other unaccounted-for variables. For the Fresno, Visalia and Bakersfield areas, the r^2 values decreased as the range of observed SEC increased (Table 1). The

Table 1. Statistics for Ground-Water SEC, TDS, and SiO_2 for the Study Areas

Parameter	*Study area (years)*	*n*	*— — Range — —* *Low*	*High*	*Median*	*Mean*	*Standard error of mean*	*Standard deviation*
SEC (mS/cm)	Fresno City wells (1977)	25	106	525	300	319	23	116
	Fresno (1950-1967)	293	139	1129	389	455	11	187
	Visalia (1950-1975)	220	130	1480	234	253	6	86
	Bakersfield (1950-1975)	261	119	2050	338	344	9	153
TDS (mg/l)	Fresno City wells	25	122	356	221	234	12	62
	Fresno	293	113	713	235	299	7	113
	Visalia	220	83	991	148	158	3	51
	Bakersfield	261	103	1726	200	214	6	93
SiO_2 (mg/l)	Fresno City wells	25	44.1	75.3	67.2	65.8	1.5	7.4
	Fresno	293	14.0	81.0	47.2	51.0	0.7	11.8
	Visalia	220	11.0	72.0	20.8	20.6	0.5	6.9
	Bakersfield	261	13.0	50.0	26.7	24.3	0.4	6.0

Table 2. Linear Regression Equations for TDS as a Function of SEC for Study Areas

Study area	*Linear regression equation*	r^2	*Standard error of estimate*
Fresno City wells	TDS = 65.5 + 0.527 SEC	0.975	9.97
Fresno	TDS = 27.2 + 0.597 SEC	0.982	15.3
Visalia	TDS = 9.32 + 0.568 SEC	0.954	11.1
Bakersfield	TDS = 14.7 + 0.579 SEC	0.907	28.5

Table 3. Multiple Regression Equations for TDS as a Function of SEC and SiO_2 for Study Areas

Study area	*Multiple regression equation*	r^2	*Standard error of estimate*
Fresno City wells	TDS = −14.7 + 0.527 SEC + 1.23 SiO_2	0.996	3.83
Fresno	TDS = − 6.4 + 0.600 SEC + 0.63 SiO_2	0.99	13
Visalia	TDS = − 3.7 + 0.520 SEC + 1.4 SiO_2	0.98	7.6
Bakersfield	TDS = − 0.62 + 0.570 SEC + 0.66 SiO_2	0.91	28

standard error of estimate for calculated TDS is also shown in Table 2.

Figure 4 shows the linear relationship between the TDS and SEC for the Fresno City wells. The 95% confidence limit about the y-intercept of 65.5 mg/l is significantly different from zero. The mean SiO_2 concentration for the area was 65.8 mg/l (Table 1). The $Si(OH)_4$ is un-ionized at the pH (6.5 to 7.5) of these waters; thus silica may be an additive quantity in the functional relationship between TDS and SEC. There was no significant linear correlation between the ground-water SEC and the SiO_2 concentration, as should be expected.

The addition of SiO_2 as another independent variable to form multiple regression equations (Table 3) for estimating TDS did not significantly change the regression coefficient for the SEC variable (Tables 2 and 3).

Examination of the coefficient of determination (r^2), coefficient of multiple determination (R^2), and standard error of the estimated value (Tables 2 and 3) indicates the inclusion of SiO_2 in the regression analysis improved the predictability of the TDS regression model for the Fresno City well field, the standard error of the estimate for TDS was reduced from 9.97 to 3.83 mg/l, and for the Visalia area the standard error of estimate was reduced from 11.1 to 7.6 mg/l. The standard error of estimate for the Fresno area was reduced from 15.3 to 13 mg/l, while for the Bakersfield area the reduction was nil.

Table 4 presents a comparison of measured and estimated TDS using simple linear regression equations with SEC as the only independent variable and multiple regression equations with SEC and SiO_2 as the independent variables. Data for this comparison illustration were obtained by random selection of 10 ground-water samples from the large data base for each study area. For these samples, the TDS was estimated by simple regression models presented in Table 2 and the multiple regression models presented in Table 3 and compared with the measured TDS. The inclusion of SiO_2 concentration in the regression models did not always produce for individual samples a lower percent difference between measured and estimated TDS, but on the average, inclusion of SiO_2 in the regression models reduced the mean difference from 4.6% to 2.8% (Table 4).

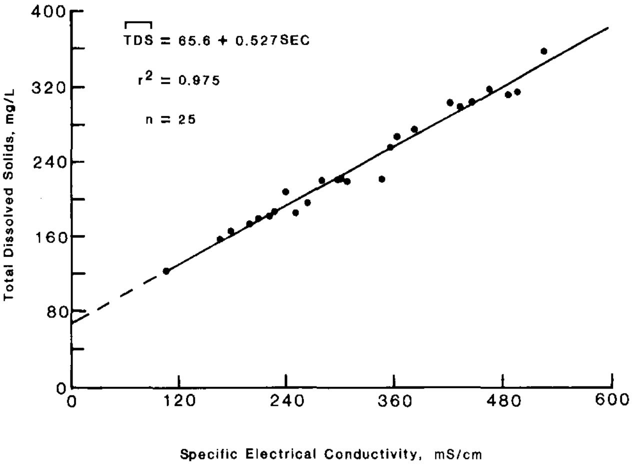

Fig. 4. Total dissolved solids as a function of specific electrical conductivity for the Fresno City well field (1977).

Table 4. Comparison of Estimated TDS from Regression Models with Measured Values

Study area	Sample number for study area	Measured			TDS (mg/l) estimated by regression using		Percent difference with respect to measured	
		SEC (mS/cm)	SiO_2 (mg/l)	TDS (mg/l)	SEC	SEC + SiO_2	TDS, estimated by SEC	TDS, estimated by SEC + SiO_2
Fresno (n = 293)	98	422	56	275	279	282	1.5	2.6
	19	470	48	305	308	306	1.0	0.3
	80	841	48	535	529	528	1.1	1.3
	103	714	55	456	453	457	0.7	0.2
	272	749	59	484	474	480	2.1	0.8
	176	450	61	293	295	302	0.7	3.1
	194	214	63	173	155	162	10.4	6.4
	204	213	65	175	154	162	12.0	7.4
	219	229	36	147	164	154	11.6	4.8
	115	370	54	243	248	250	2.1	2.9
Visalia (n = 220)	103	226	26	148	142	150	4.1	1.4
	10	186	15	119	118	114	0.8	4.2
	7	182	15	104	116	112	11.5	7.7
	39	335	24	202	206	204	2.0	1.0
	88	192	19	128	122	123	4.7	3.9
	206	278	13	156	172	159	10.3	1.9
	163	191	17	117	121	119	3.4	1.7
	144	195	15	118	124	119	5.1	0.8
	73	174	9	100	111	99	11.0	1.0
	60	171	16	107	110	108	2.8	0.9
Bakersfield (n = 261)	193	392	28	247	242	241	2.0	2.4
	69	600	26	370	362	359	2.2	3.0
	219	268	26	178	170	169	4.5	5.1
	16	244	15	139	156	148	12.2	6.5
	84	289	24	179	182	180	1.7	0.6
	210	324	21	201	202	198	0.5	1.5
	156	295	22	182	186	182	2.2	0.0
	39	475	29	283	290	289	2.5	2.1
	24	224	17	129	144	138	11.6	6.7
	91	318	26	201	199	198	1.0	1.5
							Mean = 4.6%	Mean = 2.8%

QUALITY CHANGES WITH DEPTH

The change in SEC, TDS, and SiO_2 with soil depth was investigated at the Leaky Acres Recharge Facility. The recharge water is surface water from the Gould Canal. The SEC, TDS, and SiO_2 of the percolating water increased with depth (Table 5) during recharge in these alluvium sediments. As the water passes through about 19 m (62 ft) of siliceous material, the solution approaches saturation with $Si(OH)_4$ for this near neutral pH water. Table 6 presents the regression equations for the water quality parameters as a function of depth to 18.7 m. The SEC increased on the average 2.26 mS/cm per metre of depth and SiO_2 increased on the average 1.36 mg/l per metre of depth under steady-state recharge conditions at Leaky Acres.

Table 5. Surface- and Ground-Water Quality Parameters at Leaky Acres Ground-Water Recharge Facility (1978)

Sampling site	Sampling depth (m)	SEC (mS/cm)	TDS (mg/l)	SiO_2 (mg/l)
Basin 2B	0	30	26.7	5.4
Tile line	1.5	43	38.3	10.9
Shallow well	4.0	47	45.7	14.5
Observation wells	18.7	77	63.6	32.7

Table 6. Linear Regression Equations for SEC, TDS, and SiO_2 as a Function of Sampling Depth (SD) at Leaky Acres Ground-Water Recharge Facility

Linear regression equation	r^2
SEC = 35.6 + 2.26 SD	0.995
TDS = 33.3 + 1.69 SD	0.884
SiO_2 = 7.7 + 1.36 SD	0.981

SUMMARY

The ground-water SEC, TDS, and SiO_2 data in this study were obtained from existing Federal and State agency lists. Some measurements were also made on ground-water samples from the Fresno City wells in our laboratory under known quality control conditions. Regression equations for TDS as a function of SEC and for TDS as a function of SEC and SiO_2 were determined for four study areas in the eastern San Joaquin Valley. Total dissolved solids can be estimated from either SEC or both SEC and SiO_2 by these regression models with acceptable error. Thus, the need for determining TDS by the time-consuming standard procedure for the ground-water areas studied can be reduced.

This study demonstrates that the regression model's predictability was improved by inclusion of SiO_2 in areas of high SiO_2 concentration (>45 mg/l). The SiO_2 concentration in the ground water was independent of salinity but is dependent upon the geological origin of the sedimentary deposits. This fact is illustrated by ground-water quality differences beneath three different alluvial fans on the east side of the San Joaquin Valley in California.

The approach used in this study can be used in other ground-water quality studies where TDS data are desired. Once a regression model has been made for the functional relationship between TDS and SEC or TDS and SEC plus SiO_2, from measured quantities of the parameters for a given ground-water hydrologic area, the model can then be used to estimate quickly TDS with acceptable error.

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