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Original article

Deriving Mathematical Relationships Between Electrical Conductivity and Concentrations of Some Minerals in Groundwater: A Case Study in the Mediterranean Region of Turkey

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Abstract

The quality and quantity of water varies from place to place and time to time. Therefore, supply of fresh water is a limiting factor for irrigated agriculture in arid and semi-arid regions of the world, including Mediterranean region although irrigation and fertilizers are two of the major inputs of modern agriculture in the region. Pollution from anthropogenic sources or activities degrades the quality of freshwater, lessening its usefulness. In this regard, irrigated agriculture has negative impacts on surface and groundwater resources. Staple objectives of this study are two-fold: a) to derive mathematical forms of relationship between electrical conductivity and concentrations of some minerals in groundwater, b) to bring those relationships into the use in areas where shallow water table with poor quality is dominant and only EC measurements are available. In line with those objectives, the study was conducted in an irrigated catchment, covering an area of 9 495 ha, located in the Lower Seyhan Plain irrigation project area, in the Mediterranean region of southern Turkey. A total of 362 groundwater samples were collected from 105 drainage observation wells with the depth of 4-m in winter, spring and autumn in 2016 and 2017. Electrical conductivity (EC, dS m-1) and concentrations (meq L-1) of major ions, i.e. calcium and magnesium (Ca+Mg), sodium (Na), potassium (K), chloride (Cl), carbonate (CO3), bicarbonate (HCO3) and sulfate (SO4), were determined in the lab by following standard methods. Then, total dissolved solids (TDS in mg L-1) concentration in each was calculated by summing up the major ion concentrations considered. Correlation and regression analysis was performed to derive mathematical forms of relationship between EC and TDS, and other ion concentrations. Analysis results showed that a strong linear mathematical relationship existed between TDS and EC, and Na with the determination coefficient (R2) greater than 93 percent (r≥0.95). Surprisingly the relationship between EC and Cl was found to be in the form of quadratic (R2=0.97). On the other hand, although the association between EC and Ca+Mg was linear and weak (R2=0.71), ANOVA results lead us to conclude that the relationship was statistically significant (α=0.05). Contrary to the expectations, no statistically significant relationship existed between EC and the remaining ion concentrations. Mathematical forms of the relationships between EC and mineral ion concentrations may be used to derive additional information regarding groundwater quality in agricultural areas where drainage observation wells are available and EC measurements are taken for granted.

Keywords: Irrigated agriculture, drainage observation well, water table, groundwater quality, Lower Seyhan Plain (ASO).

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INTRODUCTION

Regardless of its source, both quality and quantity of waters are subject to vary from place to place and time to time (Hoffman, 2010). Therefore, supply of fresh water is a limiting factor for irrigated agriculture in arid and semi-arid regions of the world, including Mediterranean region although irrigation and fertilizers are among the two major inputs of modern agriculture in the region. Pollution from anthropogenic sources or activities degrades the quality of freshwater, lessening its usefulness. Agriculture demands fresh water for irrigation and generates irrigation return flows (IRFs) of inferior quality. Concordantly, IRFs have posed a threat to the aquatic environments and water resources (Boyd, 2015). Additionally, it is inevitable that large amount of water leaks through the root-zone during irrigation applications and contributes to the shallow water table or deep groundwater body (Cetin, 2020). As definitively pointed out by Hanson et al. (2006) and Hiscock and Bense (2014), the process repeats itself and degrades water quality. In this regard, as accepted universally, irrigated agriculture has inherently negative impacts on the quality of surface and groundwater resources (NRCS, 1997) although irrigation is a must. On the other hand, chemical and biochemical interactions between groundwater and the geological materials of soils and rocks provide a wide variety of dissolved constituents which are either inorganic or organic. Hiscock and Bense (2014) clearly indicated that other important considerations include the varying composition of rainfall and atmospheric dry deposition over groundwater recharge areas, the modification of atmospheric inputs by evapotranspiration, differential uptake by biological processes in the soil zone and mixing with seawater in coastal areas.

In terms of drainage engineering and crop yield, the depth of groundwater and its chemical composition or concentration of constituents is of prime importance (Hoffman, 2010). Concentration is a measure of the relative amount of the dissolved constituent to water. In this regard, the principal dissolved components of groundwater in agricultural areas consist of the eight major ions (Boyd, 2015), consisting of cations {sodium (Na), calcium (Ca), magnesium (Mg), potassium (K)} and anions {chloride (Cl), carbonate (CO_3), bicarbonate (HCO_3) and sulfate (SO_4)}. These cations and anions normally comprise over 90% of the total dissolved solids content (Hiscock and Bense, 2014), regardless of whether the water is dilute rainwater or has salinity greater than seawater. On the other hand, introduction of contaminants into groundwater from human activities can result in some normally minor ions reaching concentrations equivalent to major ions. For example, excessive application of nitrogenous fertilizers or poor fertilizer management can raise nitrate concentrations in the vadose zone and groundwater to the critical levels. Apart from these, electrical conductivity of water, i.e. salinity, and total dissolved solids are the stable quality indicators of groundwater. The degree of salinization of groundwater -expressed as the total dissolved solids (TDS in mg L^{-1}) content or electrical conductivity (EC in dS m^{-1})- is a widely used method for categorizing quality status of surface waters and groundwaters. Hanson et al. (2006) and Hoffman (2010) emphasized that a simple determination of TDS helps one to determine the hydro-chemical characteristics of a regional aquifer. Equally, measuring the EC of a solution will also give a relative indication of the amount of dissolved salts, made possible by the fact that groundwater is an electrolytic solution with the dissolved components present in ionic form. On the other hand, it is expensive and time consuming to collect groundwater samples and determine major ion concentrations in the lab. However, in situ EC measurements may be done easily by using a mobile EC-meter in the field. Furthermore, for any investigation, it is possible to relate the measured concentration of constituent in groundwater as well as the TDS value to the electrical conductivity. The established relationship will be very useful to estimate the likely value of the specific constituent. However, the problem is that such a relationship is, for the most part, currently unavailable. Staple objectives of this study are two-fold: a) to derive mathematical forms of relationship between electrical conductivity and concentrations of some minerals in groundwater, b) to bring those relationships into the use in areas where shallow water table with poor quality is dominant and only EC measurements are available.

MATERIALS and METHODS

Study Area and Data

Study area is located in the Mediterranean region of southern Turkey (Figure 1). Characteristic Mediterranean climate type of with warm, dry summers and cool, mild winters is dominant in the study site. Therefore, irrigation has been practiced in the region for a long time. Shallow water table of inferior quality and salinity are among the irrigation induced on-site and off-site problems in the Lower Seyhan Plain (LSP) irrigation project area in which the study area is located. As seen in Figure 1, main, secondary and tertiary drainage canals of machine-constructed exits in the area. Drainage canals provide the service of agricultural drainage in order to get rid of irrigation induced problems such as water logging, soil salinity and alkalinity, high water table, low crop yields etc.

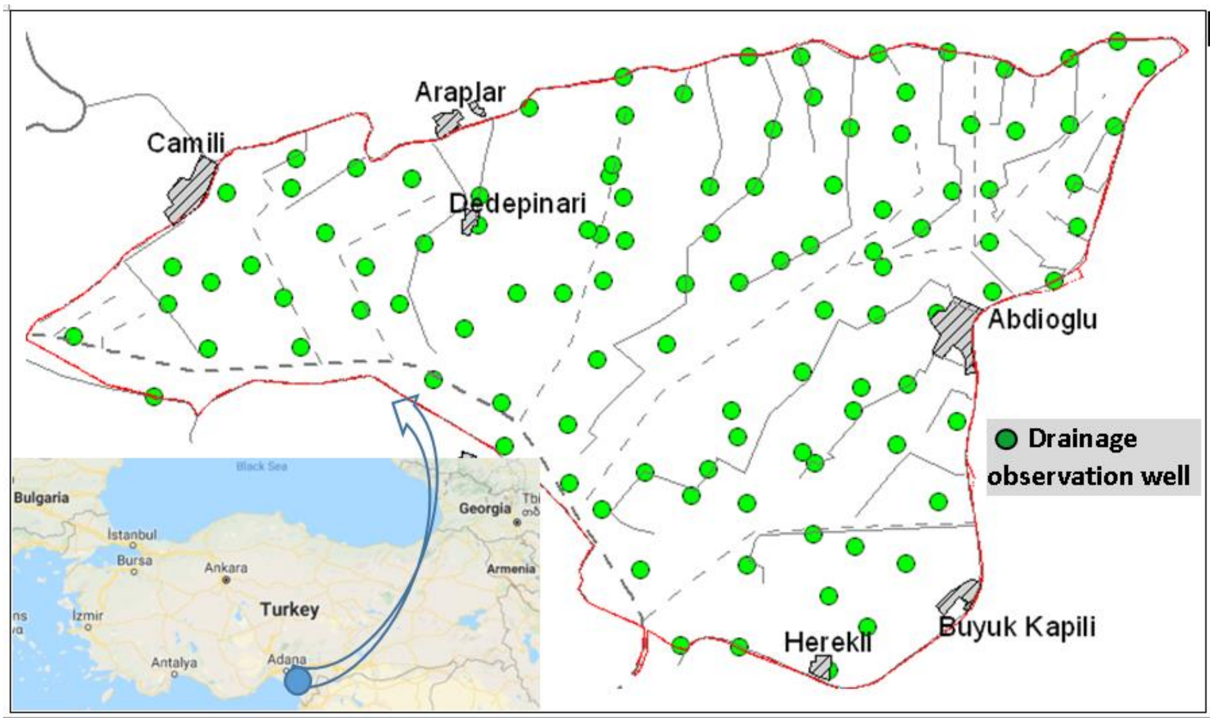

Figure 1. Location of the study area in Turkey and spatial distribution of groundwater sampling points, i.e. drainage observation wells

Study area consists of 9 495 ha of agricultural lands with deep alluvial soils of rich in clay-contents deposited by the Seyhan and Ceyhan rivers. In the study catchment, there exist 105 drainage observation wells with the depth of 4-m (Figure 1). In line with the objectives of the study, a total of 362 groundwater samples were collected from drainage observation wells in winter, spring and autumn of 2016 and 2017.

Methods

Groundwater samples were pre-processed for electrical conductivity (EC, dS m^{-1}) measurements and chemical analysis in the lab. Measurements of concentrations of major ions (meq L^{-1}), i.e. calcium and magnesium (Ca+Mg), sodium (Na), potassium (K), chloride (Cl), carbonate (CO3), bicarbonate (HCO_3) and sulfate (SO_4) as well as EC determinations, were done in the lab by following standard methods given in Boyd (2015). Then, each concentration in the unit of meq L^{-1} was converted to the unit of mg L^{-1} for the total dissolved solids (TDS) concentration calculation by Bilgin (2015). EC values were measured by using an EC-meter. Na and K ion concentrations were determined by a flame photometer, the remaining ions by titration. The sodium adsorption ratio (Hanson et al., 2006; Hoffman, 2010), SAR of (meq L^{-1})0.5 unit, of each groundwater sample were calculated as:

$$SAR=\frac{[Na]}{\sqrt{\frac{[Ca]+[Mg]}{2}}} \quad (1)$$

where [Na], [Ca] and [Mg] are the concentrations of sodium, calcium, and magnesium, respectively, expressed in milliequivalents per liter (meq L^{-1}).

Based on Hanson et al. (2006), total dissolved solids (TDS) concentration in each groundwater sample were, in turn, calculated by summing up cation and anion concentrations in the unit of mg L^{-1}. The Pearson correlation coefficient between some variable and some other variable (Li et al., 2015) were computed to indicate casual relations. Furthermore, linear and non-linear regression analyses were performed to derive mathematical forms of a priory relationship between EC and TDS, and other ion concentrations.

RESULTS and DISCUSSION

Exploratory data analysis results

Some descriptive statistics for the groundwater quality constituents were given in Table 1. As seen from Table 1, it is clear that variability in groundwater quality parameters is indeed high. In this regard, variability of Cl concentrations was found to be the highest (CV=219%). However, the mean of pH values was about 7.97 with the lowest variability (CV=4.5%). EC, Mg, Cl, K, Na, SO4, TDS and SAR values showed rather high variabilities of CV>100%. The remaining groundwater quality parameters have variability less than CV<100%. Accept for pH values, mean, median and mod values of groundwater quality parameters showed significant differences from each other, indicating a rather skewed distribution. As seen in Table 1, coefficient of skewness for the variables varied from 1.25 to 4.94, indicating a right-skewed distribution. Mean values of EC, TDS and SAR are of 2.60 dS m^{-1}, 1702 mg L^{-1} and 4.72 (meq $L^{-1})^{0.5}$, respectively. However, it should be kept in mind that the mean values for the groundwater constituents may not be used as the representative values due to the fact that distribution of variables are not normal, but right-skewed. Nevertheless, the median values of the parameters in Table 1 may be used as the representative values for interpretations to make provision for pollution control. If we only consider average Na and Cl concentrations in the groundwater, we might conclude that degree of restriction on the use is “severe” when agricultural crops are taken into account.

Correlation analysis results

In this study, Pearson correlation coefficient, i.e. inter-correlation, between some variable and some other variable (Li et al., 2015) were computed to indicate casual relations. Correlation analysis results for the data of N=362 size were given in Table 2.

Table 3. Some descriptive statistics of groundwater quality constituents *

	pH	*EC*	*Ca+Mg*	*Ca*	*Mg*	*CO_3*	*HCO_3*	*Cl*	*K*	*Na*	*SO_4*	*TDS*	*SAR*
Mean	7.97	2.596	12.98	4.52	8.47	1.43	7.16	12.34	0.10	13.44	5.80	1701.88	4.72
Standard Error of the Mean	0.02	0.176	0.64	0.19	0.50	0.05	0.19	1.42	0.01	1.21	0.38	100.38	0.32
Median	7.95	1.474	9.21	3.58	5.66	1.31	6.35	2.72	0.04	4.94	3.30	1064.61	2.28
Mode	7.93	2.520	5.33	3.05	3.16	0.65	7.74	1.36	0.03	0.04	0.00	-	-
Standard Deviation	0.36	3.349	12.15	3.63	9.58	1.04	3.67	27.08	0.19	22.93	7.24	1909.89	6.16
Kurtosis	0.36	10.998	17.53	10.26	17.68	2.47	7.47	15.70	30.51	12.11	9.34	12.16	9.68
Skewness	0.45	3.151	3.64	2.82	3.77	1.25	1.77	3.75	4.94	3.28	2.56	3.24	2.67
Range	2.14	20.671	94.02	26.09	75.59	6.54	31.83	189.64	1.78	159.22	55.46	11815.61	40.80
Minimum	7.07	0.229	1.50	0.00	0.44	0.00	1.14	0.10	0.00	0.04	0.00	271.02	0.02
Maximum	9.21	20.900	95.52	26.09	76.04	6.54	32.97	189.73	1.79	159.26	55.46	12086.63	40.82
Sample Size (*N*)	362	362	362	362	362	362	362	362	362	362	362	362	362
Confidence Level(95.0%)	0.04	0.346	1.26	0.38	0.99	0.11	0.38	2.80	0.02	2.37	0.75	197.41	0.64
CV(%)	**4.5**	**129.0**	**93.6**	**80.3**	**113.1**	**72.8**	**51.2**	**219.4**	**196.6**	**170.6**	**124.9**	**112.2**	**130.6**

***** Units of anions and cations are in meq L^{-1}, EC in dS m^{-1}, TDS in mg L^{-1}, SAR in $(meq\ L^{-1})^{0.5}$

Table 2. Correlation matrix (Pearson r) of groundwater quality parameters (Underlined figures stand for correlations greater than 0.6)

	EC	*Ca+Mg*	*Ca*	*Mg*	*CO3*	*HCO3*	*Cl*	*K*	*Na*	*SO4*	*TDS*	*SAR*
EC	1.00											
Ca+Mg	**0.85**	1.00										
Ca	0.50	**0.78**	1.00									
Mg	**0.88**	**0.97**	**0.61**	1.00								
CO3	0.22	0.03	-0.12	0.08	1.00							
HCO3	0.42	0.22	0.06	0.26	0.55	1.00						
Cl	**0.98**	**0.84**	0.47	**0.88**	0.12	0.32	1.00					
K	0.03	0.07	0.17	0.03	0.00	0.04	0.00	1.00				
Na	**0.96**	**0.70**	0.32	**0.77**	0.31	0.47	**0.94**	0.01	1.00			
SO4	0.58	**0.65**	0.57	**0.61**	0.16	0.10	0.48	0.16	0.57	1.00		
TDS	**0.99**	**0.85**	0.51	**0.88**	0.26	0.45	**0.96**	0.05	**0.97**	**0.65**	1.00	
SAR	**0.79**	0.40	0.08	0.48	0.46	0.55	**0.74**	0.01	**0.89**	0.44	**0.80**	1.00

It should be kept in mind that correlations apply to pairs of variables. If more than 2 variables is interested in, then, the correlations between all different variable pairs should be probably taken a look at. Seeing that one of the staple objectives of this study was to derive mathematical forms of relationship between electrical conductivity and concentrations of some minerals in groundwater. It will be more logical to evaluate correlations between EC and some other variable, i.e. EC and some other variable pairs. As seen in Table 2, most of the intercorrelations are positive and remarkably high. Sample size is rather high (N=362 as seen in Table 2) in this research. Correlations higher than 0.14 were found statistically significant at the significance level of $\alpha=0.01$ and degrees of freedom df=360. Although all variables, accept for K, seem to contribute somewhat to the specific conductance of groundwater, ions of Ca+Mg, Na and Cl are the staple ones contributing to the EC with correlations varying from 0.85 to 0.98. Furthermore, Cl is the most conspicuous one among those having the correlation of r=0.98. On the other hand, correlation coefficient between EC and TDS was found to be the highest (r=0.99), i.e. almost one, meaning that the two variables are perfectly positively linearly related. Similarly, high correlation between EC and SAR (r=0.79) indicates that there exits a relationship between the variables, that if EC of groundwater at a particular location is determined, then, SAR of the sample might be estimated by using the direct relationship.

Regression analysis results

Electrical conductivity (EC) of a water sample, i.e. salinity, indicates the total concentration of all ions in a water sample. On the other hand, total dissolved solids (TDS) concentration is indicative of the degree of mineralization of freshwaters. Of the water quality parameters, EC measurements with a mobile EC-meter is an easy task and will reflect the salinity of the in-situ groundwater. However, as pointed out by Wallender and Tanji (2011), Lie et al. (2015) and the others, laboratory analysis of water quality constituents is a tedious work as well as time consuming. Provided that an acceptable relationship between EC and some other quality parameter has been established, then, the likely value of the parameter considered will be easily estimated by using the established mathematical relationship without conducting tedious laboratory work. Considering this, regression analysis was done to derive the likely relationship between EC and some other groundwater quality variables.

Regression analysis offered us statistically significant mathematical forms of the relationship between EC and some other groundwater quality variables in the linear form for a) TDS=f(EC), b) {Ca+Mg}= f(EC), c) Na=f(EC) as well as in the non-linear form for d) Cl=f(EC) and e) SAR=f(EC). Explicit functions of relationships are given in Figure 2 for TDS, {Ca+Mg}, Na and Cl. Not surprisingly, as seen in Figure 2, the relationship between EC and TDS, Na, and {Ca+Mg} is in the linear form which corresponds to the correlation analysis results. However, the relationship between EC and {Ca+Mg} is not as strong as expected due to the high variability in the data (Figure 2b). On the other hand, although not linear, the relationship between EC and Cl was explicitly defined with a quadratic function with rather high determination coefficient (R2=0.98 in Figure 2c). More surprisingly, the functional relationship between SAR and EC differed from the others having a fourth degree polynomial with the coefficients of a=2.383E-01, b=7.543E-01, c=7.962E-01, d=-1.321E-01 and e=5.799E-03 (R2=0.82). It should be kept in mind that those relationships are only valid for 0.20 dS $m^{-1} \leq$ EC $\leq$22.00 dS m^{-1}. Regression analyses results led us to conclude that groundwater constituents of TDS, {Ca+Mg}, Cl, Na and SAR in the study area as well as in the Lower Seyhan Plain might be estimated from in situ electrical conductivity measurements.

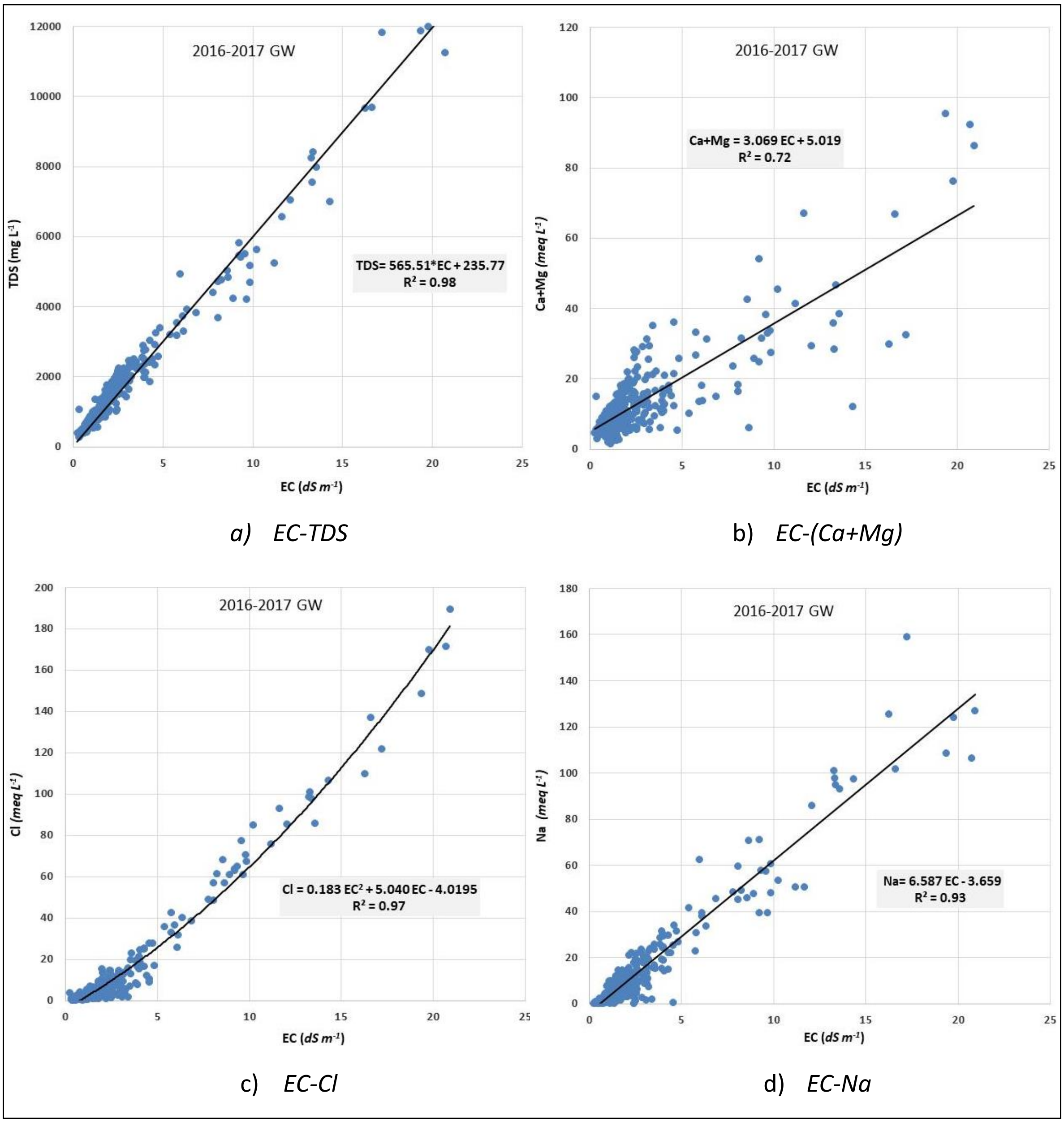

Figure 2. Relationship between electrical conductivity and some other groundwater quality variables. Relationship is only valid for 0.20 dS m-1 ≤ EC ≤22.00 dS m-1

Conclusion and Recommendations

Based on the research results obtained from this study, the following conclusions might be drawn and recommendations might be done:

- Groundwater quality constituents showed rather high variability in the agricultural catchment. Irrigation practices which are anthropogenic might have accelerated the spatial variability in water quality.
- Ionic concentrations of mineral constituents in shallow water table, i.e. groundwater, increase as specific conductance of the water increase and vice versa, either linearly or non-linearly.
- A unique relationship exists between electrical conductivity (EC) and total dissolved solids (TDS) as well as calcium plus magnesium {Ca+Mg}, chloride (Cl), sodium (Na) and sodium adsorption ratio (SAR).
- Regression analyses results might be used in practice to estimate immediately TDS, {Ca+Mg}, Cl, Na and SAR values by using in situ electrical conductivity measurements to be done in the study area and also in the in the Lower Seyhan Plain irrigation area.

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