Original Research

The Effects of Large Borate Deposits on Groundwater Quality

Arzu Çiçek[1], Recep Bakiş[2], Alper Uğurluoğlu[3], Esengül Köse[4], Cem Tokatli[5]*

[1]Applied Environmental Research Centre, Anadolu University, Eskişehir, Turkey
[2]Department of Civil Engineering, Anadolu University, Eskişehir, Turkey
[3] Institute of Science, Anadolu University,Eskişehir, Turkey
[4]Department of Environmental Protection and Control, Osmangazi Vocational School, Eskişehir Osmangazi University, Eskişehir, Turkey
[5]Department of Laboratory Technology, Ipsala Vocational School, Trakya University, İpsala/Edirne, Turkey

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Abstract

Seydisuyu Basin, which contains very important agricultural areas and boron deposits of Turkey, is located in Eskişehir province. In this paper, the groundwater quality of Seydisuyu Basin was evaluated by using some physiochemical (temperature, conductivity, salinity, and demanded oxygen) and chemical (boron and arsenic) parameters. Groundwater samples were collected seasonally (2011-12) from 14 wells from the Seydisuyu Basin and all of the data obtained experimentally were compared with national and international drinking and usage water standards. Also, cluster analysis (CA) was applied to the results to classify the stations according to the contents of arsenic and boron levels by using the Past package program, factor analysis (FA) was applied to the results to classify the affective factors on groundwater quality, and Pearson Correlation Index was applied to the results to determine the relations of parameters by using the SPSS 17 package program. According to data, arsenic and boron accumulations of wells were higher than the drinking water limits specified by the Turkish Standards Institute (TS266), European Communities (EC), and World Health Organization (WHO) Drinking Water Standards. According to the results of FA, three effective factors that explain 76.36% of the total variance was detected and arsenic-boron contents of groundwater were positively loaded with the second factor, named as "Boron Works and Environmental Factor." According to results of CA identified by using arsenic and boron accumulations, station 1, which was the closest well to the boron facility, showed the highest distance and lowest similarity with the other stations.

Keywords: arsenic, boron, groundwater quality, Seydisuyu Basin, multivariate statistic

Introduction

Arsenic and boron are not only significant hazards for surface water but also for groundwater. More than one hundred million people worldwide face the risk of arsenic poisoning because of naturally occurring arsenic in groundwater [1].

Turkey has 70% of the total boron reserve of the world and the most important borate deposits of Turkey are located in Kırka County of Eskişehir province, which constitutes our study area [2]. It is known that boron contents of geological structure significantly affect the arsenic levels and one of the most important uses of arsenic is as a pesticide due to its high toxicity [3]. Toxic effects of arsenic may interact with sulfhydryl groups of proteins and enzymes.

*e-mail: tokatlicem@gmail.com

The presence of 0.01 mg/L concentration of inorganic arsenic in food and water is dangerous to human health. It has mortal effects that contain 0.60 mg/L arsenic. Sixty percent of drinking water in Turkey is provided from groundwater [4]. Seydisuyu Basin, a sub basin of the Sakarya River Basin, was chosen as the research area for the investigation of groundwater contamination levels.

Seyitgazi Basin, which contains important agricultural areas and the most important boron deposits of Turkey, is located around Eskişehir province. In addition to the geological structure of the basin, Eti Boron Works and agricultural activities are important sources of boron and arsenic in groundwater. The aim of this study is to determine the arsenic and boron concentrations of Seydisuyu Basin and evaluate the water quality by using some statistical techniques and compare the data with national and international drinking water standards. When the location of the study area was considered, it can be clearly understood that the determination of arsenic and boron levels in groundwater of Seydisuyu Basin has a vital importance for ecosystem and human health.

Material and Method

Study Area

Seydisuyu Basin is one of the most important agricultural and mining areas of Turkey. It is located in Eskişehir Province in the Central Anatolia Region between 38.0851-39.0361 north latitude and 30.0161-31.0071 east longitudes [5].

The surface area of Seydisuyu Basin is 1816.10 km^2 and drained by Seydisuyu Stream, which has a length of 121.84 km. Groundwater samples were taken from seasonal periods in 2011-12 from wells used for drinking and irrigation water in the basin. The water samples were collected from 14 stations (wells) in different locations, including Kırka, Seyitgazi, and Mahmudiye districts of Eskişehir province. Coordinates and locations of stations were given in Table 1. Map districts of Eskişehir and study area were given in Fig. 1.

Chemical and Physicochemical Analysis

Physicochemical analysis (temperature, dissolved oxygen, salinity, and conductivity) were determined by using a "Hydrolab DS5 Multiparameter Sonde (Hach Hydromet)" device during the field studies.

The volume of one liter groundwater samples were taken at each sampling point (well) and were adjusted to pH 2 with 2 ml of HNO_3 being added to each. Arsenic and boron levels in water samples were determined by ICP-OES (Varian 720 ES). The element analyses in water samples were recorded as mean triplicate measurements [6, 7].

Statistical Analysis

Cluster Analysis was applied to the results by using the Past package program. Pearson Correlation Index and Factor Analysis were applied to the results using the SPSS 17 package program.

Results and Discussion

Annual averages of results of physicochemical and chemical analysis with minimum, maximum, mean, and

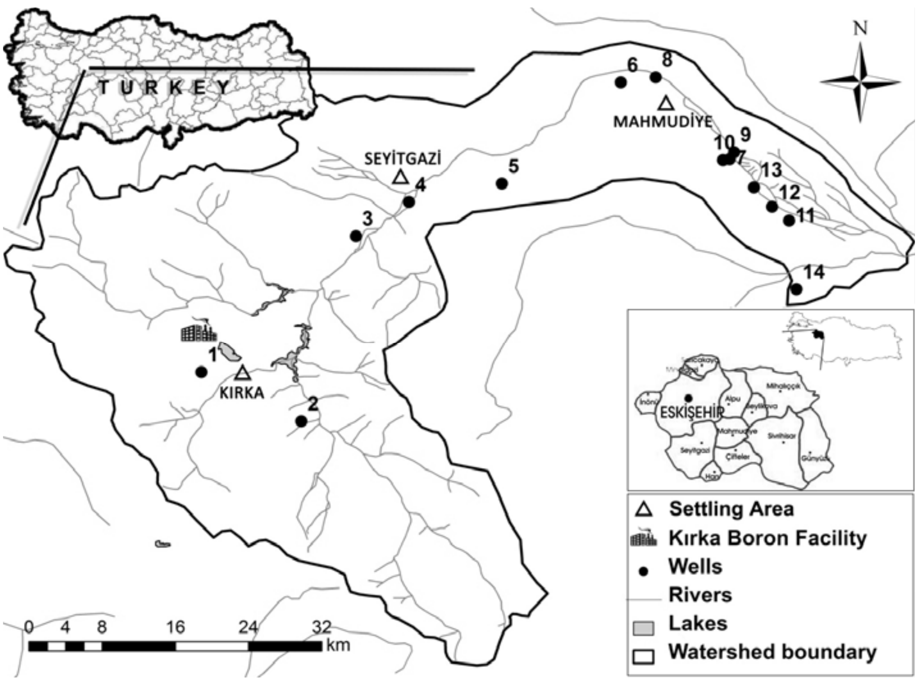

Fig. 1. Study area (sampling points, Seydisuyu Basin, and districts of Eskişehir province).

Table 1. Location properties of stations.

Wells	Coordinates		Location
	latitude	longitude	
1	39.27687N	30.47783E	Kırka District
2	39.22866N	30.57604E	Karaören Village
3	39.41094N	30.62988E	Kesenler Vilage
4	39.44451N	30.68197E	Seyitgazi District
5	39.46267N	30.77316E	Doğançayır Village
6	39.56195N	30.89019E	Yeşilyurt Village
7	39.48658N	30.99699E	Mahmudiye District
8	39.56689N	30.92443E	Hamidiye Village
9	39.49330N	31.00157E	TJK Stud Farm
10	39.48563N	30.99065E	Mahmudiye District
11	39.42622N	31.05550E	TİGEM Stud Farm
12	39.43978N	31.03883E	TİGEM Stud Farm
13	39.45891N	31.02101E	TİGEM Stud Farm
14	39.35887N	31.06268E	Çifteler District

standard deviation values are given in Table 2. Seasonal arsenic and boron accumulations with limits of drinking water are given in Fig. 2. The highest B accumulations were determined in station 1. (12.99 mg/L in summer season) and the lowest B accumulations were determined in station 5 in all seasons. The highest recorded As level was determined in station 11 as 0.15 mg/L in summer season.

The relationships between temperature, conductivity, salinity, dissolved oxygen, arsenic, and boron levels in groundwater were determined by using Pearson Correlation Index (n = 56 for all parameters). It was found that the relations between conductivity and salinity were directly proportional at the 0.01 level and the relations between arsenic and boron were directly proportional at the 0.05 level in groundwater of Seydisuyu Basin. As and B are often correlated as they are both soluble minerals found in hydrothermal-volcanic deposits [8].

Factor analyses (FA) was used to determine the effective varifactors on groundwater of Seydisuyu Basin by using correlated variables. Eigenvalues higher than one were taken as criterion for evaluating the principal components required to explain the sources of variance in the data.

The percentage variance counted, cumulative percentage variance, and component loadings (unrotated and rotated) are given in Table 3. According to rotated variance of the cumulative percentage, three factors explain 76.36% of the total variance.

The parameter loadings (> 0.5) for three components before and after rotation are given in Table 4. Liu [9] classified the factor loadings as: strong (> 0.75), moderate (0.75-0.50), and weak (0.50-0.30), according to loading values.

First factor (F1, named "Nutrient Factor") explains 34.1% of total variance and is related to the variables of conductivity and salinity values of groundwater. All parameters were strongly positively loaded with this factor. As it is known, nutrient salts strongly affect the values of conductivity and salinity in the water and in a study performed in North Greece to determine the water quality, conductivity was strongly positively loaded with Nutrient Factor (0.82) [10, 11].

The second factor (F2, named "Boron Works and Environmental Factor") explains 22.4% of total variance and is related to the variables of boron and arsenic values of groundwater. All parameters were strongly positively loaded with this factor.

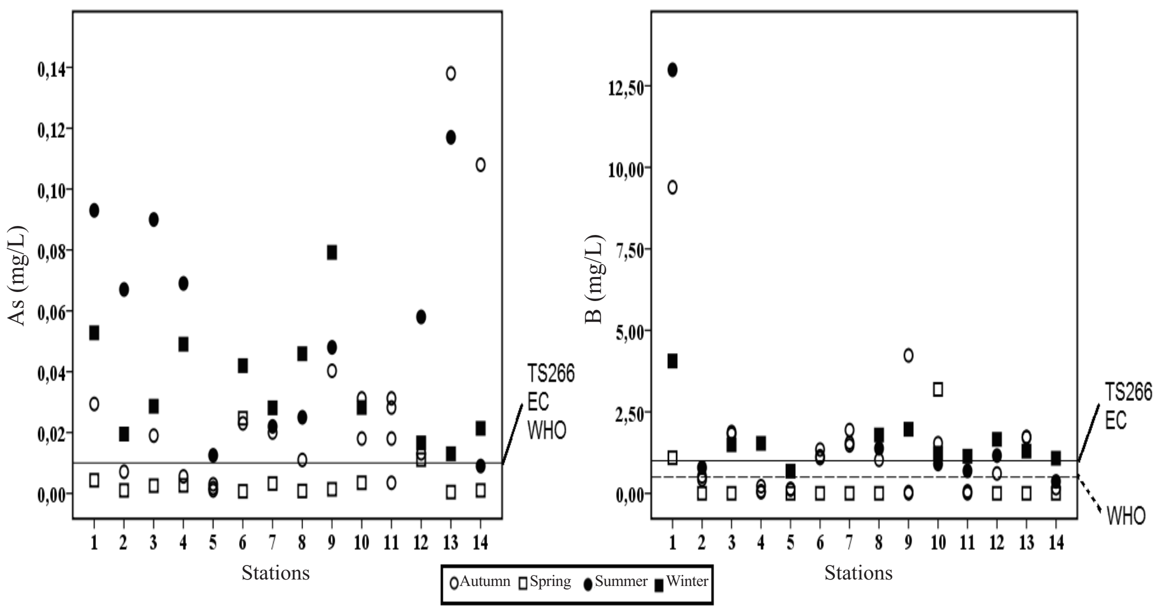

Fig. 2. Seasonal As and B accumulations of groundwater in Seydisuyu Basin and limit values for drinking water (TS266 – Turkish Standards Institute, EC – European Communities, WHO – World Health Organization).

Table 2. Annual averages of physicochemical and chemical parameters with minimum, maximum, and standard deviation levels.

Parameters		Station (Well) Numbers													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temp (C0)	min	11.920	7.060	8.040	12.010	8.720	10.210	14.020	13.420	13.750	7.360	15.040	15.110	12.850	24.290
	max	14.790	16.489	15.400	14.980	16.200	17.400	15.200	17.050	15.360	20.160	21.140	17.460	17.690	25.000
	mean	13.570	12.527	12.210	13.863	14.185	15.133	14.723	14.853	14.585	15.093	17.588	16.490	14.678	24.610
	SD	1.207	3.948	3.097	1.356	3.649	3.328	0.526	1.547	0.659	5.448	2.676	1.017	2.115	0.296
DO (mg/L)	min	4.060	3.280	1.720	4.100	7.130	5.380	2.920	3.920	2.130	2.110	4.260	3.480	3.720	5.660
	max	6.452	8.630	6.750	6.370	7.860	7.380	4.320	7.200	5.570	6.930	7.100	7.310	10.310	6.040
	mean	5.526	5.068	4.513	5.335	7.438	6.701	3.433	5.613	4.193	4.538	5.365	6.065	6.595	5.808
	SD	1.030	2.417	2.330	0.935	0.305	0.938	0.648	1.349	1.467	2.246	1.221	1.790	2.762	0.165
Cond (mS/cm)	min	338.0	207.6	614.0	637.0	462.3	1236.0	1143.1	560.0	1168.4	1017.1	737.0	738.1	771.7	881.4
	max	612.3	679.1	926.1	1022.8	879.0	1360.5	1375.7	1699.2	2909.0	1414.0	1267.1	1002.0	1199.0	1046.6
	mean	497.1	473.2	842.6	845.5	614.4	1308.0	1274.5	1101.6	2186.1	1224.4	1088.6	849.5	1066.3	970.1
	SD	117.6	234.2	152.6	163.2	185.6	52.1	96.9	468.5	780.7	197.8	243.7	110.7	199.2	67.9
Sal 0‰	min	0.210	0.130	0.400	0.400	0.230	0.650	0.600	0.290	0.620	0.530	0.380	0.380	0.400	0.460
	max	0.310	0.350	0.480	0.540	0.460	0.720	0.730	0.900	1.570	0.750	0.670	0.520	0.630	0.550
	mean	0.262	0.247	0.458	0.459	0.315	0.690	0.675	0.578	1.173	0.644	0.573	0.442	0.560	0.508
	SD	0.043	0.114	0.039	0.063	0.102	0.029	0.054	0.251	0.427	0.110	0.133	0.058	0.108	0.037
As (mg/L)	min	0.004	0.001	0.003	0.003	0.001	0.001	0.003	0.001	0.001	0.003	0.002	0.011	0.000	0.001
	max	0.093	0.067	0.090	0.069	0.013	0.042	0.028	0.046	0.079	0.031	0.150	0.058	0.138	0.108
	mean	0.045	0.024	0.035	0.032	0.005	0.023	0.018	0.021	0.042	0.020	0.047	0.025	0.067	0.035
	SD	0.038	0.030	0.038	0.033	0.005	0.017	0.011	0.020	0.032	0.013	0.069	0.022	0.070	0.049
B (mg/L)	min	1.090	0.000	0.000	0.034	0.000	0.000	0.000	0.000	0.000	0.900	0.000	0.000	0.000	0.000
	max	12.990	0.790	1.880	1.533	0.681	1.346	1.945	1.792	4.230	3.190	1.139	1.660	1.730	1.079
	mean	6.883	0.434	1.298	0.465	0.235	0.891	1.242	1.051	1.560	1.716	0.473	0.858	1.187	0.402
	SD	5.326	0.328	0.882	0.717	0.304	0.605	0.854	0.766	2.003	1.017	0.542	0.715	0.816	0.476

Temp – Temperature, DO – Demanded Oxygen, Cond – Conductivity, Sal – Salinity, As – Arsenic, B – Boron
min – minimum, max – maximum, mean – average, SD – standard deviation

Table 3. Extracted values of various FA parameters (loadings of total variance).

Component	Extraction Sums of Squared Loadings (unrotated)			Rotation Sums of Squared Loadings (rotated)		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.090	34.828	34.828	2.047	34.109	34.109
2	1.330	22.169	56.997	1.344	22.403	56.512
3	1.162	19.371	76.368	1.191	19.856	76.368

Table 4. Values of component matrix and rotated component matrix (factor loadings of parameters).

Parameters	Component matrix			Rotated component matrix		
	1	2	3	1	2	3
Conductivity	0.980			0.991		
Salinity	0.978			0.989		
Arsenic		0.804			0.787	
Boron		0.701			0.775	
Temperature			-0.853			0.824
Dissolved oxygen			0.519			-0.626

The third factor (F3, named "Geologic and Climatic Factor") explains 19.8% of total variance and is related to the variables of temperature and dissolved oxygen values of groundwater. As it is known, climatic factors and geologic structure are significantly affective on water temperature and oxygen solubility decreases with increasing temperature [11]. Temperature parameter was strongly positively loaded and dissolved oxygen parameter was moderately negatively loaded with this factor.

Cluster analyses (CA) was used to determine the similarity groups between the stations. The diagram of CA calculated by using arsenic and boron levels in groundwater of Seydisuyu Basin is given in Fig. 3. According to the CA, the highest similarity was determined between stations of 3 and 7 (94.7%) and the lowest similarity was determined between stations of 1 and 5 (6.6%). Also, station 1 formed a distinct group from all other stations according to As and B accumulations. Station 1 was located on the Kırka District and it was the closest station to the Eti Boron Mine (Fig. 1). A significant increase of boron level was determined in groundwater of this station, especially in summer season (12.99 mg/L). So it can be understood from the data that the Eti Boron Mine significantly affects groundwater quality, especially around Kırka District.

Mulivariety statistical analysis are used widely to assess water quality and provide valuable data [12-14]. In a study performed on Uluabat Lake in Turkey and similar to the results of the present study, FA and CA were used to evaluate water quality. According to FA, 77.35% of variances explained by 3 factors and microbiological factor that best explains the observed variances had 32.34% of total variace. According to CA, hierarchical cluster analysis grouped 12 sampling sites into 2 clusters of similar water quality [15].

According to drinking water standards specified by the Turkish Standards Institute, European Communities and the World Health Organization, arsenic and boron accumulation in groundwater of Seydisuyu Basin were much higher than the drinking water limits (>0.01 mg/L for As; >0.5 mg/L (WHO) and >1 mg/L (TS266, EC) for B) and dangerous for human health (Fig. 2) [16-18]. In West Bengal, India, it is estimated that more than one million Indians are drinking arsenic-laced water and tens of millions more could be at risk in areas that have not been tested for contamination. Analysis of 20,000 tubes revealed that 62% have arsenic at levels above the permissible exposure limit in drinking water of 0.01 mg/L, with some as high as 3.7 mg/L [19]. In Seydisuyu Basin, 92% of groundwater has arsenic at levels above the limit values in drinking water.

In a study performed in Emet Stream, where important boron deposits of Turkey are located, it was reported that As and B accumulations extremely exceeded the limit values for drinking water, especially around the stations close to the boron mine (maximum As: 1 mg/L and maximum B: 74 mg/L) [20]. In contrast to the data reported by Tokatlı and current values of Seydisuyu Basin, as it is known that

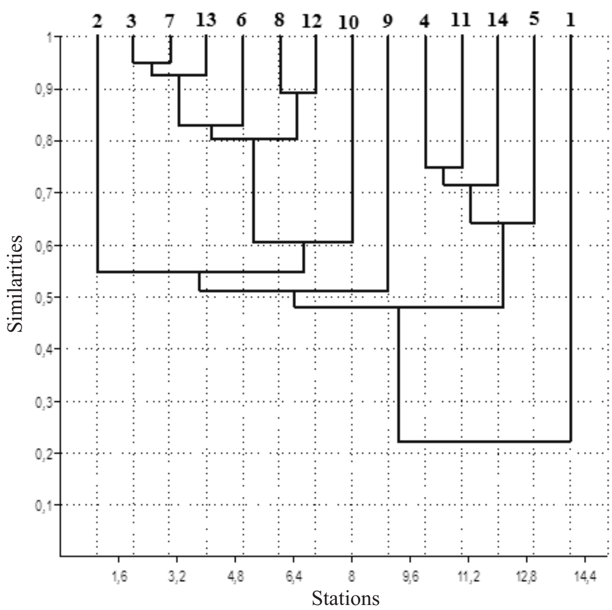

Fig. 3. Tree diagram of CA (a visual summary of the clustering processes).

groundwater is far more likely to contain high levels of arsenic than surface water [21]. According to data, it can be said that if we compare the two large boron deposit areas, Emet region is exposed to point discharge more than Seydisuyu Basin in terms of arsenic. In another study performed around the Emet-Hisarcık districts (Turkey), arsenic levels in groundwater of all study regions (0.01-0.56 mg/L) and boron levels in groundwater of close stations (0.59-4.34 mg/L) to the boron mine exceeded the limit values for drinking water [22]. If we compare the groundwater quality of the Emet-Hisarcık region and Seydisuyu Basin, mining activities in Seydisuyu adversely affect the groundwater quality more than Emet-Hisarcık regions in terms of boron (maximum B in Seydisuyu Basin: 12.99 mg/L). Additionally, in the present study As and B accumulations of groundwater in stations far from the Kırka Boron Facility also were over the limit values. These results reflect that the geological structure is an affective factor on accumulations of arsenic and boron in groundwater of Seydisuyu Basin.

The concentration of arsenic in natural surface and groundwater is generally about 0.001 mg/L, but may exceed 1 mg/L in mining areas or where arsenic levels in soil are high. Surveys of U.S. drinking water indicate that about 80% of water supplies have less than 0.002 mg/L of arsenic, but 2% of supplies exceed 0.02 mg/L of arsenic [21]. In Seydisuyu Basin, about 78% of groundwater exceeds 0.02 mg/L of arsenic. The process of arsenic entering groundwater depends upon local geology, hydrogeology, geochemical characteristics of the aquifer, climate changes, and human activity. As it is known, pesticides are important for releasing arsenic to the environment [23]. So it is thought that intensive agricultural activities in the Seydisuyu Basin are effective at As accumulation in groundwater.

Arsenic concentrations in groundwater samples collected from 73 wells in 10 counties in southeast Michigan in the USA in 1997 ranged from 0.0005 to 0.278 mg/L, with an average of 0.029 mg/L [24]. Average As levels in groundwater of Seydisuyu Basin (0.031 mg/L) were higher than the averages of Michigan.

Reported boron concentrations in groundwater in the San Joaquin Valley ranged from 0.14 to 120 mg/L with a median concentration of about 4 mg/L [25, 26]. In Seydisuyu Basin the average boron concentrations of groundwater is 1.33 mg/L and boron levels are significantly lower than the San Joaquin Valley.

As a result, our study indicates that in addition to the geological structure of the basin and mining activities, taking part of important agricultural lands in the Seydisuyu Basin causes an increase of arsenic and boron levels in groundwater.

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