

IMPACT OF INDUSTRY ON GROUND WATER CONTAMINATION: A CASE STUDY IN KONYA CITY, TURKEY

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ABSTRACT

Having developed rapidly in recent years, Konya, one of Turkey's most significant industrial cities, has been hosting production activities in sectors such as glass, chemistry, mining, metal and machine in the factories 96% of which located in the third Organized Industrial Zone. In common environmental agenda, it was suggested that wastewater stemming from increased industrial diversity and some geological lithology can create environmental problems, including groundwater contamination. In this study, to characterize dry and rainy period, samples were collected from 11 wells so as to determine effects of wastes in the area on groundwater quality. The relation between industrialization and contamination was investigated in water samples, whose contents were examined for NH₃, NO₃, SO₄, B, Ca, Cl, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Sr, V, and Zn. Element distribution maps of locations where concentration rise occurred were determined in the vicinity. It was specified that SO₄, Ca, Cl, Na, Cr, Mg, Mn, Ni and Zn in samples exceeded the maximum contaminant levels according to WHO, EPA and EC standards. It was determined that water samples belonging to rainy period were contaminated more than that of dry period, which poses a threat to environment.

Keywords: contamination; environment; ground water; industry; Turkey

1. Introduction

The contamination problem in groundwater has started to be talked about in many studies due to increasing industrial development in the World (Sponza and Karaoglu, 2002; Gowd and Govil, 2008; Krlshna and Mohan, 2014). Contamination has a significant vital risk especially for people who use this water for drinking and usage. Negative results that are at a level to affect the health of people are faced due to its effect (Yildiz *et al.*, 2008). Factory wastes concerned with industrial manufacturing may have potential that may cause contamination (Nalbantcilar and Pinarkara, 2011; Nas, 1998; Arundas, 2010; Shankar *et al.*, 2008; Ullah *et al.*, 2009; Azizullah *et al.*, 2011). The fact that industrial zones cause water contamination in has been demonstrated in many samples. Moreover, numerous studies have reported water contamination originating from industrial zones (Sponza and Karaoglu, 2002; Gowd and Govil, 2008; Krishna and Mohan, 2014; Shankar *et al.*, 2008; Ullah *et al.*, 2009; Azizullah *et al.*, 2011; Krishna *et al.*, 2009; Dasaram *et al.*, 2011; Afzal *et al.*, 2014).

This study was performed in the third Organized Industrial Zone (OIZ), where 168 industrial plants are located approximately 20 km northwest of the city centre of Konya, which is situated in the central part of Turkey (Figure 1). Since a variety of industrial productions such as metallurgy, mining, food, and electronics, among many others have been conducted in the OIZ, it has been asked whether all kinds of

materials from products to the waste emerging in their productions processes contaminate the groundwater in the vicinity. This study thus aimed to determine the relationship between industrial production in the OIZ and groundwater quality. This study will provide important contributions to the water supply policy of the region as it is the first research study of its kind for this aim.

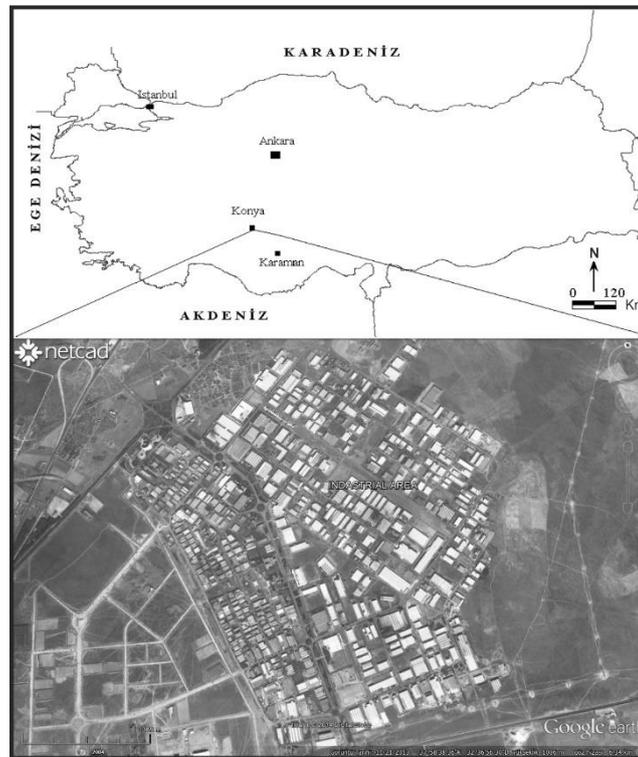


Figure 1. Location map of the study area

Geological studies of the investigation zone and the vicinity have been performed (Hakyemez *et al.*, 1992; Eren, 2001), as have various studies on groundwater quality and contamination (Nalbantcilar and Pinarkara, 2011; Ozdemir and Aydin, 1998; Nalbantcilar, 2002; Nalbantcilar and Guzel, 2006; Pinarkara, 2011), environmental problems (Nalbantcilar and Ozdemir, 2009), risks of contaminating aquifers (Nalbantcilar, 2008; Nalbantcilar *et al.*, 2009; Nalbantcilar, 2011), and the properties of industrial zone-originated waste have been conducted (Nas, 1998; Arundas, 2010). In the regions close to the study area, contamination likely to affect public health was found in the drinking water wells (Nalbantcilar, 2002; Nalbantcilar and Guzel, 2006).

The aim of this study is the establishment of physical and chemical indexes to monitor the contamination of groundwater in the OIZ. For this purpose, it is researched whether the OIZ, the source of industrial contamination determined from waste water analyzes and in which chemistry, metal and machinery factories are located, has an effect on groundwater or not.

1.1 Hydrogeology

As Figure 2 shows, the geology of the OIZ and its environment comprises Late Pleistocene formation (Konya formation) consisting of a few attached siltstones, sandstones, and conglomerates, as well as Pleistocene to Holocene formation (Aslimyayla formation) with the properties of salty swamps and consisting of salt, gypsum, and intermediate-level mudstones (Hakyemez *et al.*, 1992; Eren, 2001).

While conglomerates are badly sorted and semi-spherical in Konya formation and though their coarse-grained sandstones have high permeability, their siltstones exhibit impermeable properties. Therefore, this formation is classified as less permeable. The total porosity of Konya formation ranges from 26% to 33%; however, the addition of siltstone lowers their porosity (Pinarkara, 2011). The mudstones in

Aslimyayla formation and parallel layered gypsums are impermeable. The total porosity of Aslimyayla formation is 34% (Pinarkara, 2011), though gypsum-bearing levels in the formation lower their porosity. It has been reported that Aslimyayla formation is weak in terms of surface recharge properties, yet that Konya formation are very high in this regard (Nalbantcilar, 2002). Furthermore, their storage coefficient shows unconfined aquifer property from 0.07–0.11% (Nalbantcilar, 2002; Nalbantcilar and Guzel, 2006). The depth of the water level in the area ranges from 5–12 m.

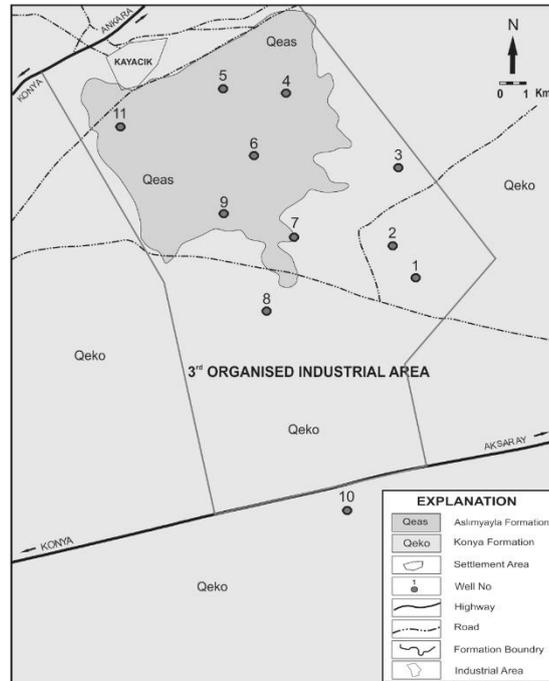


Figure 2. Geological map of the study area (modified from Hakyemez *et al.*, 1992) and the groundwater sampling wells

1.2 Properties of the OIZ

Konya's third OIZ is located in an area of about 900 ha and consists of 168 industrial plants, most of which perform production-related processes (Table 1). The work performed in these plants involves industrial sectors such as wood, glass, metal, chemistry, and mining. In fact, sectors associated with glass, chemistry, mining, metal, and machine production comprise 96% of the OIZ's total production.

Table 1. Types of sectors in the third OIZ, number of firms and their rate (Pinarkara, 2011)

Sectoral Types	Firms Number and Ratio (%)	
Wooden products and furniture industry sector	2	1
Glass industry sector	60	36
Food industry sector	4	2
Chemistry industry sector	17	10
Mining industry sector	10	6
Metal industry sector	22	13
Cellulose, paper, carton industry sector	2	1
Mass machine production, electrical machines and equipment, spare part industry sector	48	29
Textile industry sector	3	2
Total	168	100

Each day, approximately 4,000 m³ of process and domestic wastewater containing liquid waste and the

OIZ waste is transmitted to a wastewater treatment plant. Water treated there is collected in a treated water treatment pool and used to irrigate recreational fields and/or as process water in the OIZ (Arundas, 2010). Domestic and industrial solid waste from factory production also emerges, so do raw materials and temporary waste disposals fields of factories in inventory fields. These wastes are generally influenced by climatic conditions, and contamination due to rainfall can mix with groundwater directly.

While domestic wastewater emerges due to wood processing and both furniture and glass production, process wastewater emerges in other sectors and can contain Cd, Cr, Cu, Fe, N, P, Pb, and Zn (Table 2).

Table 2. Average waste water analysis values in the third OIZ (I, III, V, and VI numbered of sampling points) (Arundas, 2010)

Parameters	Wastewater Analyses				
	I	III	V	VI	Mean
EC ($\mu\text{mhos cm}^{-1}$)	18 476	8224	13 773	11 095	12 892
Cd (ppm)	0.031	0.023 6	0.027 2	0.026 8	0.027
Cr (ppm)	0.027 4	0.023 4	0.027 4	0.043 2	0.030
Cu (ppm)	0.481	0.61	1.638	1.16	0.97
Fe (ppm)	1.69	2.63	7.35	9.19	5.21
N (ppm)	9.0	10.7	12.6	21.2	13.38
Total P (ppm)	2.70	3.21	3.78	6.37	4.02
Pb (ppm)	0.568	0.760	0.94	0.693	0.74
Zn (ppm)	0.63	0.435	0.469	0.42	0.49

2. Materials and Methods

To establish the properties of the groundwater in the investigation area, 11 wells distributed over the area were identified so that they together could represent the total area (Figure 2). From August 2010 until March 2011, groundwater sampling was performed in these wells to characterize dry and rainy seasons for hydrochemical analysis.

In Water and Sewerage System Administration of Konya City Municipality (KOSKI) Water Analysis Laboratory, cation and anion analyses of the water samples filled in 1 L double-capped sterilized plastic bottles were performed according to the rules specified in the standard methods of the American Public Health Association (APHA, 1992). Trace element analyses of water samples, to which acidification was applied to achieve a $\text{pH} > 2$, were performed in Selcuk–Iltel Analytical Laboratories in Konya via inductively coupled plasma mass spectrometry.

The regions where results obtained having regional distributions and concentration rises were put forth. Moreover, the analysed results were evaluated according to WHO, EPA and EC drinking water standards. As a result, it was aimed to find out the points posing threat to the public health.

3. Hydrochemical properties of groundwater

Table 3 shows the results of dry period analyses (August 2010). The electrical conductivity (EC) of groundwater in the area ranged from $1\,389\ \mu\text{mhos cm}^{-1}$ (Sample 3) to $6\,900\ \mu\text{mhos cm}^{-1}$ (Sample 10). The total dissolved solids (TDS) of groundwater in the area ranged from 885 ppm (Sample 3) to 4 395 ppm (Sample 10). Sulphate (SO_4) concentrations ranged from 196.29 ppm (Sample 9) to 435.36 ppm (Sample 10). The amount of iron (Fe) ranged from 0.389 ppm (Sample 1) to 1.80 ppm (Sample 2), while lithium (Li) values ranged from 0.057 ppm (Sample 3) to 0.247 ppm (Sample 10). Magnesium (Mg) concentrations fell between 66.60 ppm (Sample 3) and 283.50 ppm (Sample 10), whereas nickel (Ni) fell between 0.003 ppm

(Sample 1) and 0.01 ppm (Sample 5). Strontium (Sr) concentration was defined at levels ranging from 2.40 ppm (Sample 3) to 12.20 ppm (Sample 10). In two water samples, zinc (Zn) showed concentrations ranging from 0.01 ppm (Sample 10) to 3.50 ppm (Sample 9). Meanwhile, manganese (Mn) appeared mostly concentrated in only two samples of which (Sample 1) reached 0.079 ppm. Lastly, copper (Cu) appeared in two samples only: Sample 1 (0.002 ppm) and Sample 10 (0.006 ppm). Also, the distributions of the analyses obtained from water samples collected in the study area are given in Figure 3 - 5.

Table 3. The results of dry period analyses on the water samples (in ppm; except as noted)

Sample No	1	2	3	4	5	6	7	8	9	10	11
Well coordinate (X)	467678	467414	467490	466411	465888	466157	466501	466252	465878	467055	464897
Well coordinate (Y)	4203519	4203813	4204523	4205223	4205259	4204578	4203893	4203257	4204093	4201487	4204928
pH	7.24	7.33	7.05	6.8	6.86	6.84	6.97	7.36	6.97	7.08	6.94
EC ($\mu\text{mhos cm}^{-1}$)	1 925	1 593	1 389	1 776	1 795	1 574	1 648	1 587	1 746	6 900	2 220
TDS	1226	1015	885	1131	1143	1003	1050	1011	1112	4395	1414
T Alkalinity	442	484	447	474	498	494	517	498	432	475	456
T Hardness (Fr)	73	82	71	86	90	80	82	81	87	168	90
Turbidity (NTU)	4	6.1	0.4	3.8	0.4	0.4	0.5	0.4	0.4	30.7	0.4
NH ₃	0.066	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	1.1	0.02
NO ₃	1.8	6.5	14.3	12.1	9.6	7.4	8.9	9.4	12.1	10.8	6.2
SO ₄	217.68	262.51	234.66	280.64	282.85	263.21	270.37	262.3	196.29	435.36	302.66
B	0.287	0.208	0.234	0.186	0.268	0.213	0.198	0.20	0.235	0.256	0.175
Ca	77.30	88.00	102.60	131.20	115.10	85.60	93.90	102.20	140.30	138.40	143.40
Cl	308.75	132.05	101.65	165.3	166.25	130.15	135.85	128.25	267.9	198.55	308.75
Cr	0.03	0.025	0.035	0.034	0.043	0.025	0.026	0.030	0.032	0.026	0.033
Cu	0.002	-	-	-	-	-	-	-	-	0.006	-
Fe	0.389	1.80	0.513	0.637	1.215	0.393	0.452	0.503	0.655	0.524	0.662
K	11.10	8.90	8.60	8.70	9.00	10.70	11.20	10.10	11.40	28.90	10.20
Li	0.141	0.065	0.057	0.060	0.104	0.071	0.069	0.068	0.097	0.247	0.065
Mg	103.10	73.00	66.60	77.2	76.10	77.80	81.80	74.00	83.00	283.50	96.30
Mn	0.079	-	-	-	-	-	-	-	-	0.032	-
Na	181.10	92.30	75.80	117.0	119.20	95.40	99.80	93.80	75.00	930.90	187.30
Ni	0.003	0.005	0.005	0.007	0.01	0.005	0.004	0.005	0.006	0.005	0.006
Sr	3.1	2.60	2.40	3.30	3.20	2.50	2.50	2.70	2.60	12.20	3.90
Zn	-	-	-	-	-	-	-	-	3.50	0.010	-

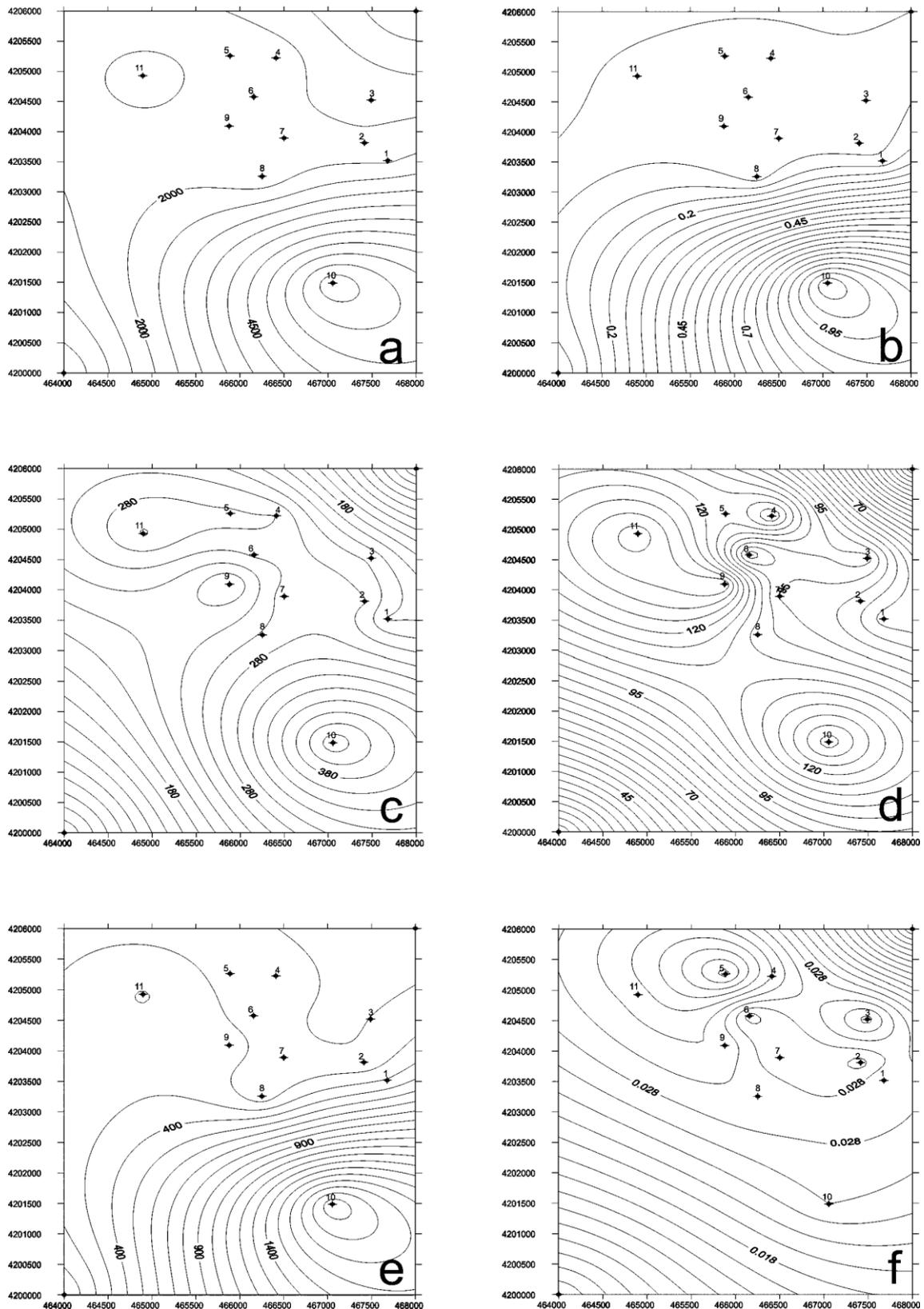


Figure 3. Iso-distribution map of EC (a) and iso-concentration maps (in ppm) of NH₃ (b), SO₄ (c), Ca (d), Cl (e), Cr (f) of the groundwater samples

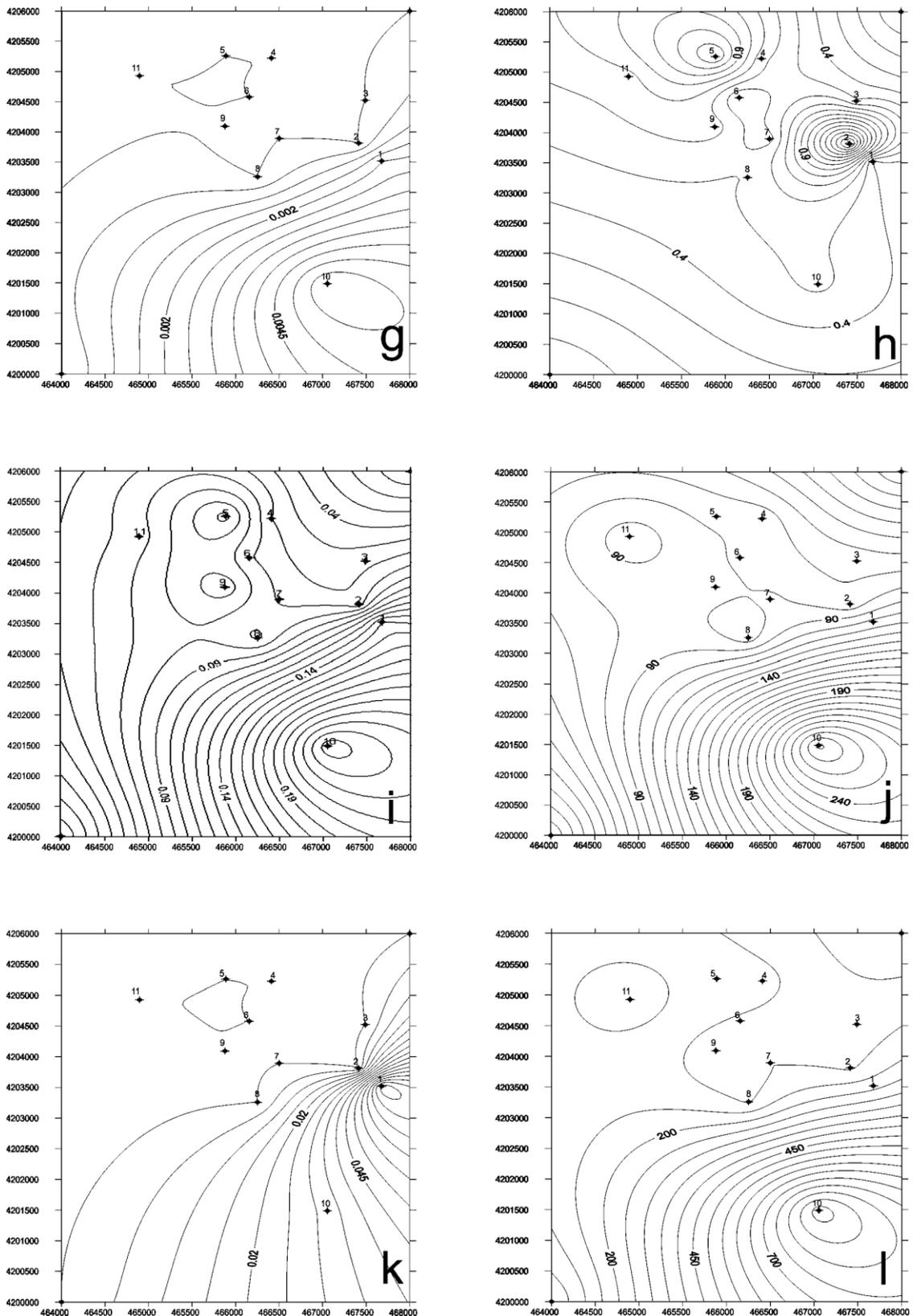


Figure 4. Iso-concentration maps (in ppm) of Cu (g), Fe (h), Li (i), Mg (j), Mn (k), Na (l) of the groundwater samples

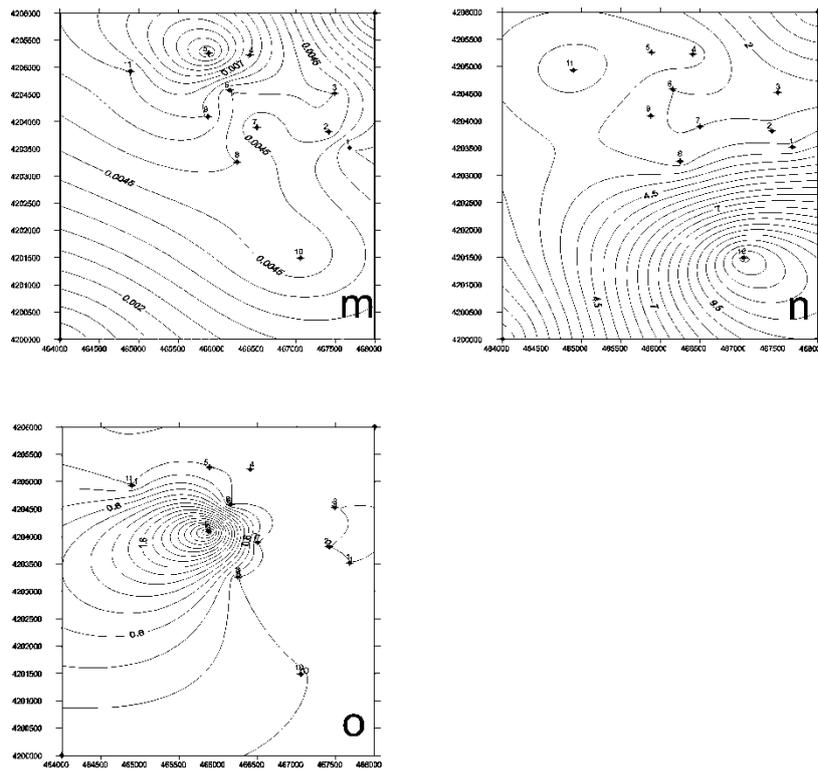


Figure 5. Iso-concentration maps (in ppm) of Ni (m), Sr (n), Zn (o) of the groundwater samples

Table 4. The results of rainy period analyses on the water samples (in ppm; except as noted)

Sample No	1	2	3	4	5	6	7	8	9	10	11
Well coordinate (X)	467678	467414	467490	466411	465888	466157	466501	466252	465878	467055	464897
Well coordinate (Y)	4203519	4203813	4204523	4205223	4205259	4204578	4203893	4203257	4204093	4201487	4204928
pH	7.16	7.21	7.01	7.04	6.76	6.8	6.83	6.82	6.9	7.1	6.95
EC ($\mu\text{mhos cm}^{-1}$)	4 380	2 177	1 842	1 942	1 930	1 860	2 032	1 610	1 899	2 610	3 042
TDS	2 790	1 387	1 173	1 237	1 229	1 185	1 294	1 025	1 210	1 662	1 938
T Alkalinity	441.75	482	492.9	502.2	492.9	487	521	478.95	437.1	500	437.1
T Hardness (Fr)	119	118	82	87	85	90	93	68	84	100	102
Turbidity (NTU)	3.9	6.2	0.93	4.6	0.4	1.2	0.7	3.03	0.6	0.6	2.6
NH ₃	0.26	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
NO ₃	3.8	8.7	4.2	5	4.7	11.2	9.3	6.8	6.7	0.7	1.4
SO ₄	358.36	281.47	263.67	275.93	304.04	259.5	283.12	208.19	180.01	415	301.11
B	0.20	0.22	0.21	0.204	0.206	0.23	0.238	0.218	0.219	0.201	0.196
Ca	138.6	125.4	194.04	205.92	229.68	127	183	162.36	194.04	218.25	221.76
Cl	940.5	235	153.45	186.12	175.23	127.3	141.5	101.97	288.09	285	653.75
Co	0.003	0.003	0.003	0.003	0.005	0.003	0.003	0.004	0.005	0.004	0.005
Cr	0.142	0.137	0.135	0.132	0.168	0.157	0.153	0.186	0.142	0.161	0.169
Cu	0.005	-	-	-	-	-	-	-	-	0.006	-
Fe	6.422	12.41	7.822	8.819	11.53	6.381	6.425	9.267	11.28	10.5	13.35
K	10.08	8.83	9.70	11.60	10.70	11.20	10.42	10.00	10.40	11.57	10.20
Li	0.353	0.038	0.032	0.31	0.027	0.044	0.041	0.049	0.079	0.03	0.028
Mg	201.71	154.92	80.44	84.15	65.59	115	113	65.59	85.39	106	111.38
Mn	0.062	-	-	-	-	-	-	0.007	0.002	-	0.055
Na	402.5	103.73	86.2	126.27	128.74	97.29	80.73	88.78	87.16	198.49	228.45
Ni	0.045	0.042	0.058	0.065	0.087	0.063	0.068	0.073	0.086	0.087	0.108
Sr	2.988	2.23	2.543	2.846	2.89	2.74	2.42	2.09	2.20	2.84	3.47
V	0.032	0.003	0.003	0.002	-	0.005	0.005	-	0.007	0.010	0.015
Zn	-	-	-	-	0.503	-	-	0.206	3.263	0.304	0.060

Table 4 shows the results of rainy period analyses (March 2011). The EC of groundwater in the area ranged from 1 610 $\mu\text{mhos cm}^{-1}$ (Sample 8) to 4 380 $\mu\text{mhos cm}^{-1}$ (Sample 1). The total dissolved solids (TDS) of groundwater in the area ranged from 1 025 ppm (Sample 8) to 2 790 ppm (Sample 1). SO_4 concentrations ranged from 180 ppm (Sample 9) to 415 ppm (Sample 10). The amount of Fe ranged from 6.381 ppm (Sample 6) to 13.35 ppm (Sample 11), while Li values ranged from 0.027 ppm (Sample 5) to 0.079 ppm (Sample 9). Mg concentrations fell between 65.59 ppm (Sample 5) and 201.71 ppm (Sample 1), whereas Ni fell between 0.042 ppm (Sample 2) and 0.108 ppm (Sample 11). Sr concentration was defined at levels ranging from 2.09 ppm (Sample 8) to 3.47 ppm (Sample 11). In five water samples, Zn showed concentrations ranging from 0.06 ppm (Sample 11) to 3.263 ppm (Sample 9). Meanwhile, Mn was attained in only four samples the concentration of which (Sample 1) reached 0.062 ppm. Lastly; Cu appeared in two samples only: Sample 1 (0.005 ppm) and Sample 10 (0.006 ppm). Also, the distributions of the analyses obtained from water samples collected in the study area are given in Figure 6 - 8.

4. Discussion

In the studies and water analyzes carried out in the scope of this study, it was observed that the industrial area, where approximately 4,000 m^3 of liquid waste is discharged and particularly metals, chemicals and machinery manufacturing exist, affect the quality of the groundwater. It was also determined that the geological features also have an effect on groundwater in the region.

4.1 Evaluation of Hydrochemical Properties and its Distribution on the Area

According to the analysis results of dry period, Sample 1 had the highest concentrations of B, Cl, and Mn; Sample 2, Fe; Sample 4, NO_3 ; Sample 5, Cr, and Ni; Sample 7, total alkalinity; Sample 8, pH; Sample 9, Zn, and NO_3 ; Sample 10, EC, total hardness, turbidity, NH_3 , SO_4 , Cu, K, Li, Mg, Na, and Sr; and Sample 11, Ca, and Cl (Table 3). In respect to the analysis results of rainy period, Sample 1 had the highest concentrations of EC, NH_3 , Cl, Li, Na, Mg, Mn, and V; Sample 2, turbidity, pH, and total hardness; Sample 4, K; Sample 5, Ca; Sample 6, NO_3 ; Sample 7, total alkalinity and B; Sample 8, Cr; Sample 9, Zn; Sample 10, SO_4 and Cu; and Sample 11, Fe, Sr, and Ni (Table 4).

According to the analysis results of dry period, the north-eastern part of the OIZ contained EC, NH_3 , SO_4 , Ca, Cl, Cu, Li, Mg, Na, and Sr in high density; the northern part, Cr, and Ni in high density; the eastern part, Fe, and Mn in high density; and in the central part, high densities of Zn. Figure 3-5 shows a concentration distribution map. In respect to the analysis results of rainy period, the eastern part of the OIZ contained Cl, Li, Mg, Mn, Na, V, and NH_3 in high density; the north-western part, Co, Fe, Ni, and Sr in high density; the south-western part, Cu and SO_4 in high density; in the area extending from the northwest to the southeast, a high density of Cr; and in the central part, high densities of Ca and Zn. Figure 6-8 shows a concentration distribution map. The area on which Ca and SO_4 focus at Figure 3 and 4 corresponds to the area where the Aslimyayla formation.

4.2 Evaluation of Water Quality

The Piper (1944) diagram was used to evaluate the water quality of groundwater samples taken from the study area (Figure 9). Also studies to use the waters for irrigation in agriculture were examined with the Wilcox (1955) diagram (Figure 10).

At the Piper diagram of the water samples in dry period, 10 numbered sample plots into 7 zone, other samples plot into 9 zone (Figure 9a). At evaluation of water analysis belonging to rainy period, 11 numbered sample plots into 6 zone, 6, 7 and 8 numbered samples plot into 5 zone and other samples plot into 9 zone (Figure 9b). The water plotting in 7. District are classified as "water, non-carbonate alkalinity of which are more than carbonate alkalinity". These waters are also waters with NaCl, NaSO_4 and KCl and "water, non-carbonate alkalinity of which are more than 50%". Alkalis and strong acids are dominant. The waters that plot into 9 zone are "mixed compound waters, none of the ions of which exceeds 50%". At waters plotting in 6. District "non-carbonate hardness is higher than 50%". These waters are the waters with CaSO_4 and MgSO_4 . At waters plotting in 5. District "carbonate hardness is higher than 50%". These waters are waters with CaCO_3 and MgCO_3 .

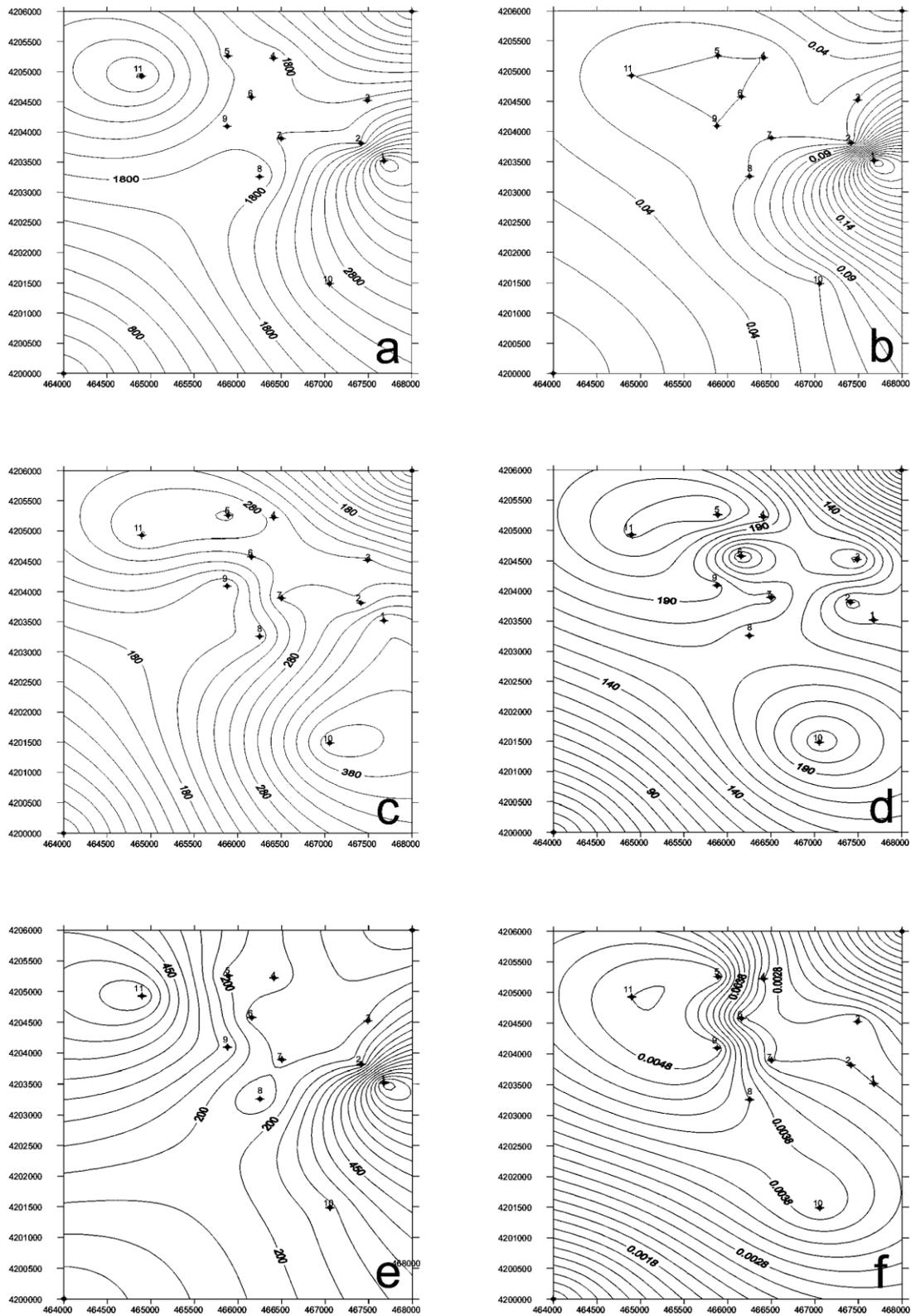


Figure 6. Iso-distribution map of EC (a) and iso-concentration maps (in ppm) of NH₃ (b), SO₄ (c), Ca (d), Cl (e), Co (f) of the groundwater samples

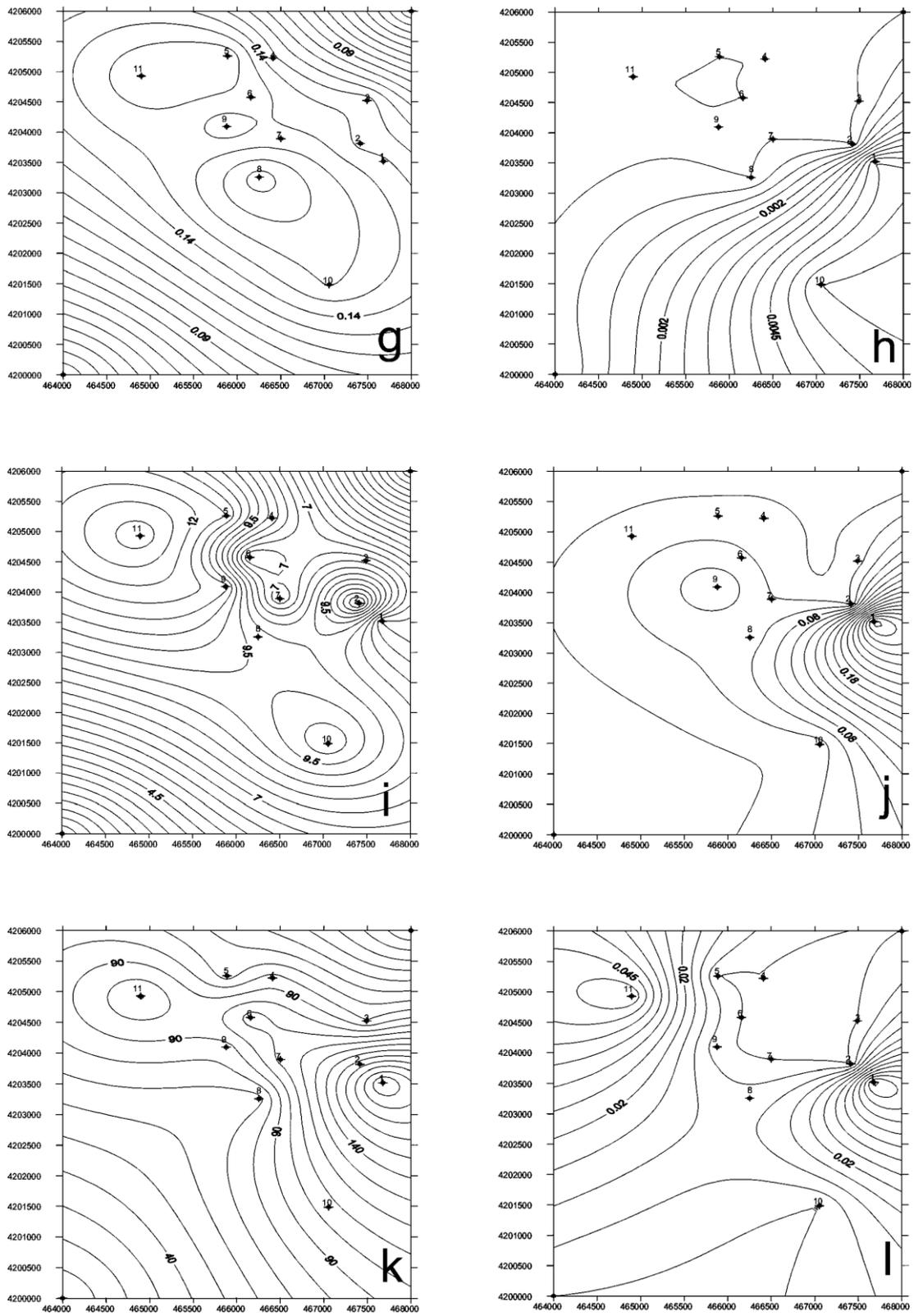


Figure 7. Iso-concentration maps (in ppm) of Cr (g), Cu (h), Fe (i), Li (j), Mg (k), Mn (l) of the groundwater samples.

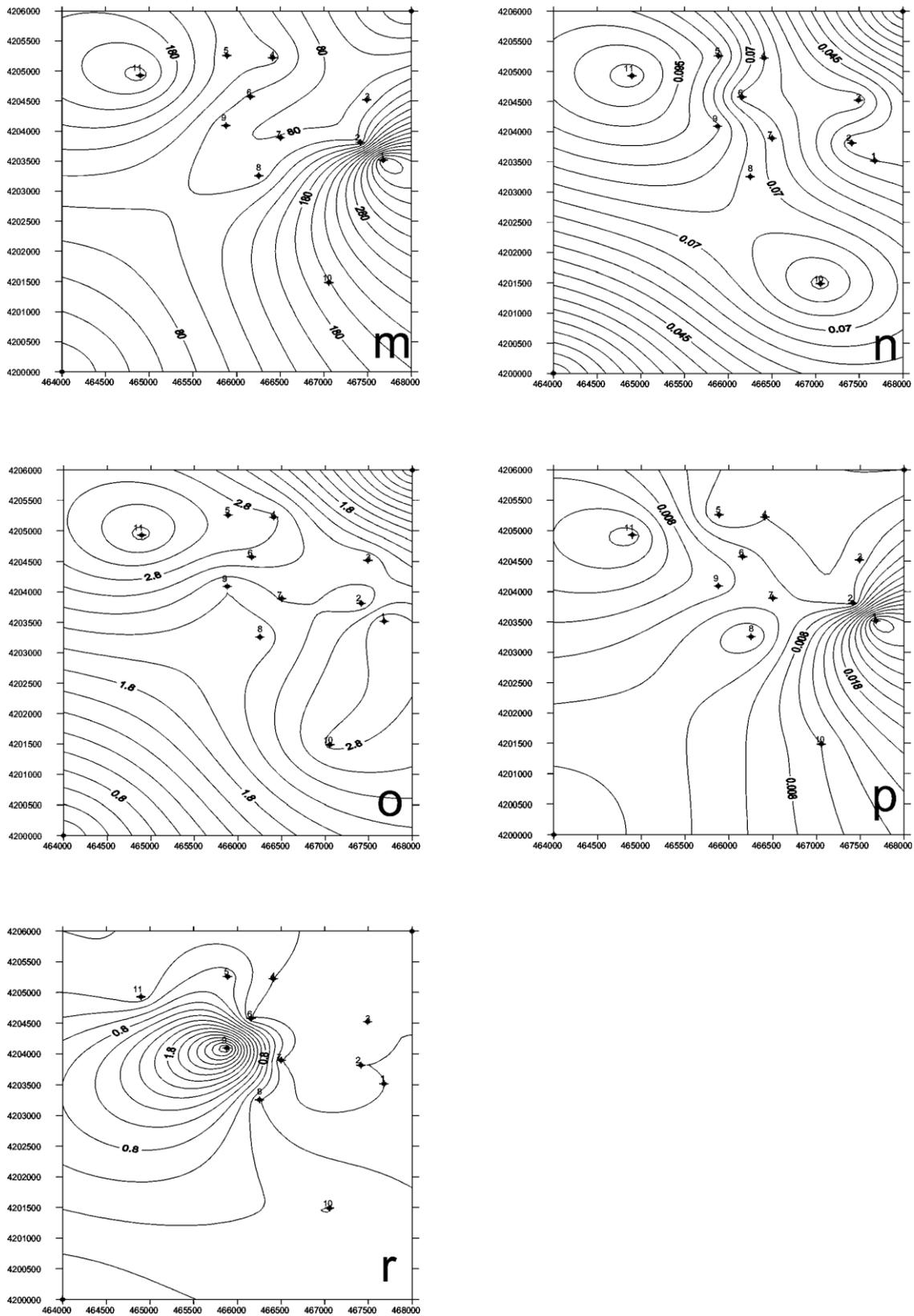


Figure 8. Iso-concentration maps (in ppm) of Na (m), Ni (n), Sr (o), V (p), Zn (r) of the groundwater samples

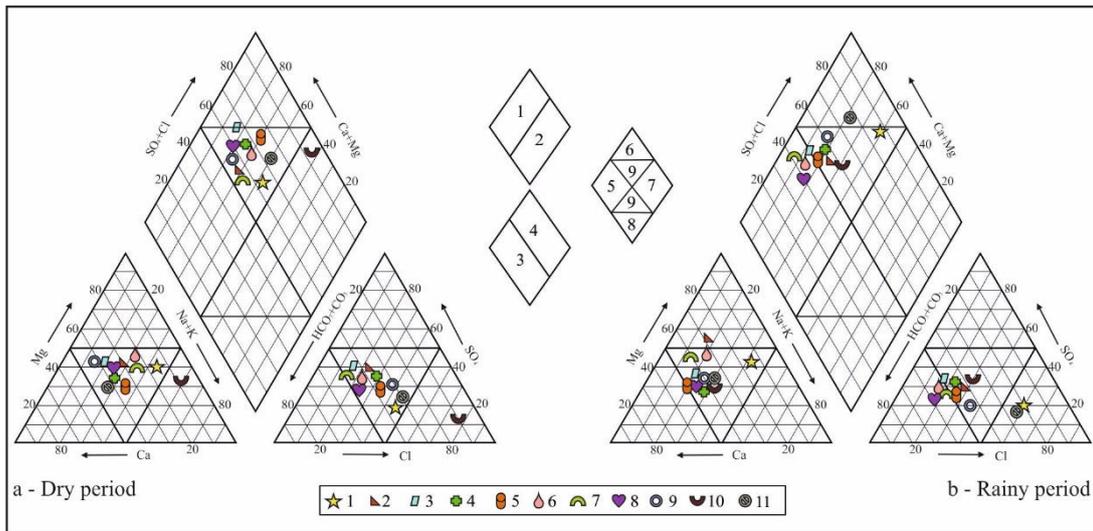


Figure 9. Piper diagram of the water samples

The Wilcox diagram distribution of water samples from dry period was made in order to evaluate the use of the waters in the study area for irrigation. Accordingly, it was determined that 10 numbered sample is classified as "not appropriate", 11 numbered sample is classified as "suspicious-not appropriate" and the other samples are classified as "well-used" for irrigation (Figure 10a). It was determined that 2, 7 and 10 numbered samples of rainy period are classified as "suspicious-not appropriate", 1 and 11 numbered samples of rainy period are classified as "not appropriate" and the other samples of rainy period are classified as "well-used" (Figure 10b).

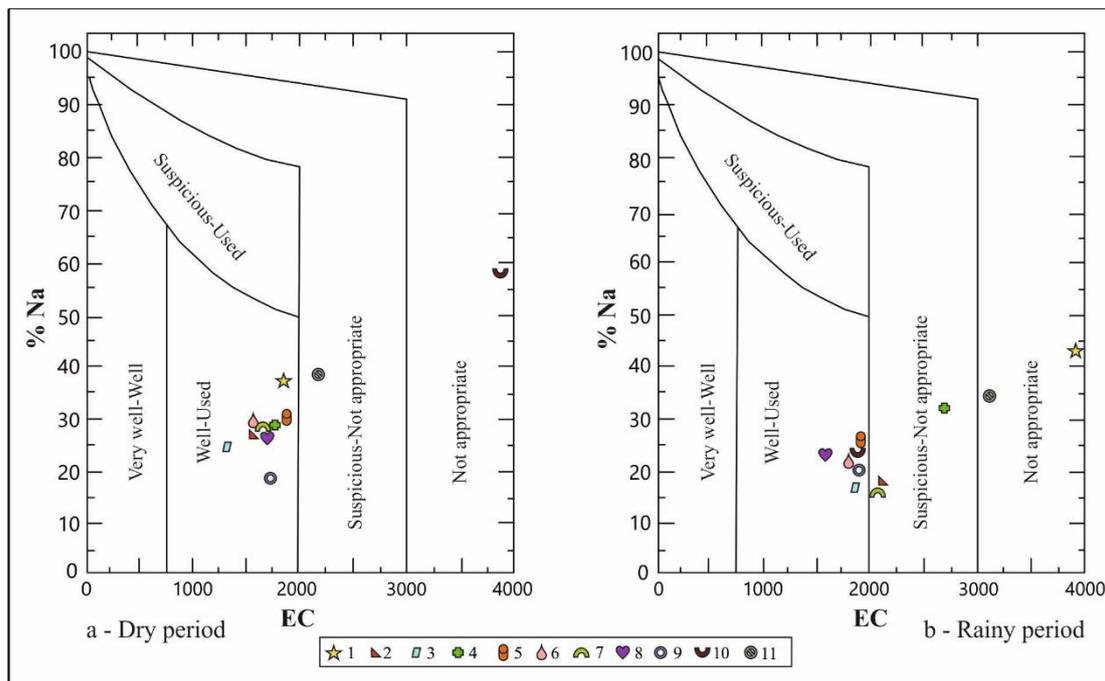


Figure 10. Wilcox diagram of the water samples

4.3 Evaluation of Contamination

The results of the two period analysis were compared in terms of potability in respect to limiting values to the maximum contamination level (MCL) according to Guidelines for Drinking-Water Quality of the World Health Organization (WHO, 2011), the National Primary Drinking Water Regulations of the U.S.

Environmental Protection Agency (EPA, 2009), and European Communities (Drinking Water) Regulations (EC, 2007) (Table 5).

Table 5. Water samples exceeding (in ppm) the guideline values of the WHO (2011), the MCL of the EPA (2009) and the indicator parameters of the EC (2007) Standards*

Elements	WHO	Sample No	EPA	Sample No	EC	Sample No
NO ₃	50		10	<u>3, 4, 9, 10</u> 6	50	
SO ₄	250	<u>2, 4, 5, 6, 7, 8, 10, 11</u> 1, 2, 3, 4, 5, 6, 7, 10, 11	250	<u>2, 4, 5, 6, 7, 8, 10, 11</u> 1, 2, 3, 4, 5, 6, 7, 10, 11	250	<u>2, 4, 5, 6, 7, 8, 10, 11</u> 1, 2, 3, 4, 5, 6, 7, 10, 11
Cl	250	<u>1, 9, 11</u> 1, 9, 10, 11	250 SMCL	<u>1, 9, 11</u> 1, 9, 10, 11	250	<u>1, 9, 11</u> 1, 9, 10, 11
Cr	0.05	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	0.1	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	0.05	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
Fe	-		0.3 SMCL	<u>1, 2, 3, 6, 7, 8, 9, 10, 11</u> 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	0.2	<u>1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11</u> 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
Mn	0.1		0.05 SMCL	<u>1</u> 1, 11	0.05	<u>1</u> 1, 11
Na	200	1, 11	200	1, 11	200	1, 11
Ni	0.02	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11	-		0.02	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
Zn	3	<u>9</u> 9	5 SMCL		-	

*Note: 1- The underlined numbers are of August 2010; while the others are of March 2011

2- SMCL: Secondary Maximum Contaminant Level of EPA (2009)

In respect to Table 5; during August 2010 period, all samples showed levels of Mg in excessive of the MCL, while nearly all samples had excessive levels of SO₄, Ca, and Fe, four samples excessive level of NO₃, three samples excessive Cl, one sample excessive Mn, and Zn. During March 2011 period all samples showed levels of Cr, Fe, and Mg in excessive of the MCL, while nearly all samples had excessive levels of Ca and Ni. Nine samples had excessive SO₄, four samples excessive Cl, two samples excessive Na, and Mn, and one sample excessive NO₃, and Zn. In summary; almost all samples had high level of concentrations of SO₄, Ca, Mg, and Fe in both periods. It was determined that Cr, Na and Ni concentrations exceeded MCL values only in rainy period.

Nitrate (NO₃) exceeds MCL limit at four samples in the dry period, at one sample in the rainy season. High NO₃ concentrations are due to the fertilizers used in agricultural activities in the dry period from the agricultural areas around the OIZ. The presence of NO₃ in the rainy period is due to the sewage system and point contamination.

The fact that Cr, Fe, Mg, and Ni originating mostly from industrial contamination exceed the MCL in nearly all samples suggests that contamination has occurred throughout the OIZ. In support of this suggestion, Co, Fe, Li, and Sr appeared in all wells, while Mn, V, and Zn appeared in some water samples in different concentrations.

Rising levels of components such as Ca, Cl, Na, and SO₄ in the OIZ's water should be seen as a result of the interaction of salty components Na and Cl, the hardness of which are quite low and which dissolve easily in water. Meanwhile, Ca and SO₄.2H₂O as components of gypsum lithology appeared in Aslımyayla formation and groundwater. As the results of the analyses showed, nearly all samples had concentration levels of Ca and SO₄ that exceeded MCL. At the same time, the EC distribution map and Ca, Cl, Na, and SO₄ concentration maps resembled each other, suggesting a naturally occurring contamination state due to the OIZ's geology and which stems from the interaction of water and rock.

4.4 Evaluation of the Statistical Analysis of the Groundwater

The analysis results of groundwater samples collected during dry and wet seasons were evaluated statistically so that they will be of two seasons (Table 6 and 8). All evaluations were realized 95% relevance level. Within this context, correlation coefficient and cluster analyses were conducted (Table 7 and 9, Figure 11 and 12).

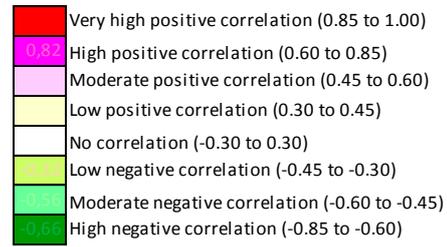
Table 6. Statistical evaluation of the water samples of dry period

	Mean	Standard Error	Standard Deviation	Test t value	Lower Limit	Upper Limit
pH	7,04	0,06	0,19	120,09	6,91	7,17
EC	2195,73	474,96	1575,25	4,62	1137,46	3254,00
TDS	1398,64	302,52	1003,33	4,62	724,59	2072,68
T Alk.	474,27	8,17	27,10	58,05	456,07	492,48
T Hard.	90,00	8,02	26,59	11,23	72,14	107,86
Turb.	4,32	2,71	8,98	1,60	-1,71	10,35
NH3	0,12	0,10	0,32	1,25	-0,10	0,34
NO3	9,01	1,04	3,46	8,64	6,69	11,33
SO4	273,50	18,62	61,75	14,69	232,02	314,99
B	0,22	0,01	0,04	20,88	0,20	0,25
Ca	110,73	7,28	24,15	15,21	94,50	126,95
Cl	185,77	22,73	75,37	8,17	135,13	236,41
Cr	0,03	0,00	0,01	18,74	0,03	0,03
Cu	0,004	0,002	0,003	2,000	-0,021	0,029
Fe	0,70	0,13	0,43	5,44	0,42	0,99
K	11,71	1,75	5,80	6,70	7,81	15,60
Li	0,09	0,02	0,06	5,59	0,06	0,13
Mg	99,31	18,69	61,98	5,31	57,67	140,95
Mn	0,06	0,02	0,03	2,36	-0,24	0,35
Na	187,96	75,16	249,29	2,50	20,49	355,44
Ni	0,01	0,00	0,00	10,17	0,00	0,01
Sr	3,73	0,86	2,85	4,34	1,82	5,64
Zn	1,76	1,75	2,47	1,01	-20,42	23,93

In the groundwater samples of dry period: TDS-EC; T.Hard-EC and TDS; Turb.-EC, TDS and T.Hard.; NH₃-EC, TDS, T.Hard. and Turb.; SO₄-EC, TDS, T.Hard. and NH₃; K-EC,TDS, T.Hard., Turb. and NH₃; Li- EC,TDS, T.Hard., Turb., NH₃ and K; Mg- EC,TDS, T.Hard., Turb., NH₃, SO₄, K and Li; Na- EC,TDS, T.Hard., Turb., NH₃, SO₄, K, Li and Mg; Sr- EC,TDS, T.Hard., Turb., NH₃, SO₄, K, Li, Mg and Ni element pairs have very high positive correlation (Table 7). Only Cl-T.Alkalinity and Cl-NO₃ element pairs show a high negative and moderate negative correlation in order.

Table 7. Correlation coefficients between the element pairs of the water samples of dry period

	pH	EC	TDS	T Alk.	T Hard.	Turb.	NH3	NO3	SO4	B	Ca	Cl	Cr	Fe	K	Li	Mg	Na	Ni	Sr
pH	1,00																			
EC	0,04	1,00																		
TDS	0,04	1,00	1,00																	
T Alk.	-0,05	-0,03	-0,03	1,00																
T Hard.	-0,04	0,98	0,98	0,06	1,00															
Turb.	0,16	0,97	0,97	-0,01	0,94	1,00														
NH3	0,08	0,99	0,99	-0,01	0,97	0,98	1,00													
NO3	-0,35	0,10	0,10	-0,03	0,19	0,08	0,14	1,00												
SO4	-0,09	0,88	0,88	0,31	0,90	0,84	0,86	0,11	1,00											
B	0,16	0,29	0,29	-0,30	0,21	0,31	0,33	-0,17	-0,01	1,00										
Ca	-0,42	0,44	0,44	-0,32	0,52	0,30	0,36	0,49	0,41	-0,22	1,00									
Cl	-0,03	0,17	0,17	-0,63	0,11	0,07	0,08	-0,49	-0,06	0,23	0,37	1,00								
Cr	-0,38	-0,26	-0,26	-0,20	-0,21	-0,35	-0,30	0,31	-0,19	0,24	0,34	0,11	1,00							
Fe	0,23	-0,14	-0,14	0,17	-0,06	-0,02	-0,15	-0,09	-0,01	-0,02	-0,06	-0,19	0,13	1,00						
K	0,07	0,98	0,98	-0,01	0,96	0,95	0,99	0,10	0,82	0,32	0,36	0,15	-0,37	-0,23	1,00					
Li	0,13	0,91	0,91	-0,14	0,86	0,89	0,91	-0,09	0,67	0,63	0,24	0,32	-0,17	-0,17	0,92	1,00				
Mg	0,07	1,00	1,00	-0,06	0,96	0,96	0,99	0,05	0,85	0,33	0,38	0,21	-0,30	-0,19	0,99	0,93	1,00			
Na	0,06	1,00	1,00	-0,03	0,97	0,97	0,99	0,06	0,88	0,31	0,39	0,17	-0,27	-0,16	0,98	0,91	1,00	1,00		
Ni	-0,53	-0,08	-0,08	0,16	0,06	-0,15	-0,12	0,38	0,11	0,01	0,48	-0,09	0,78	0,41	-0,19	-0,12	-0,15	-0,11	1,00	
Sr	0,02	1,00	1,00	-0,02	0,98	0,96	0,99	0,12	0,90	0,28	0,46	0,16	-0,22	-0,13	0,97	0,89	0,99	1,00	-0,04	1,00



EC, NH₃, SO₄ show positive correlation in correlation analyses of dry season analyses, and In pair concentration maps belonging to Li, Mg, Na and Sr groundwater table also, In pair concentration maps belonging to Li, Mg, Na and Sr groundwater table exhibit similar distributions (Figure 3, 4 and 5). At the points of investigation area where groundwater concentration changes were observed, the pairs having very high correlations possess similar decrease and increase (Table 7). However, the fact that Mg-Cr pairs have concentration changes in separate points supports negative correlation between these element pairs (Figure 3 and 4) (Table 7). In Figure 3 and 4, it was determined that Ca and Fe elements having scattered curves in correlation analyses did not possess any correlations (Table 7).

Table 8. Statistical evaluation of the water samples of rainy period

	Mean	Standard Error	Standard Deviation	Test t value	Lower Limit	Upper Limit
pH	6,96	0,05	0,15	150,06	6,86	7,07
EC	2302,18	240,55	797,83	9,57	1766,19	2838,17
TDS	1466,36	153,25	508,28	9,57	1124,90	1807,83
T Alk.	479,35	8,58	28,46	55,86	460,23	498,47
T Hard.	93,45	4,64	15,38	20,16	83,12	103,79
Turb.	2,25	0,59	1,97	3,80	0,93	3,57
NH ₃	0,08	0,02	0,06	4,30	0,04	0,12
NO ₃	5,68	0,98	3,24	5,81	3,50	7,86
SO ₄	284,58	19,31	64,05	14,74	241,55	327,61
B	0,21	0,00	0,01	53,15	0,20	0,22
Ca	181,82	11,49	38,12	15,82	156,22	207,43
Cl	298,90	78,86	261,56	3,79	123,18	474,62
Co	0,00	0,00	0,00	13,67	0,00	0,00
Cr	0,15	0,01	0,02	29,71	0,14	0,16
Cu	0,01	0,00	0,00	11,00	0,00	0,01
Fe	9,47	0,76	2,52	12,46	7,78	11,17
K	10,43	0,25	0,82	41,97	9,87	10,98
Li	0,09	0,04	0,12	2,62	0,01	0,17
Mg	107,56	12,25	40,63	8,78	80,27	134,86
Mn	0,03	0,02	0,03	2,01	-0,02	0,08
Na	148,03	29,34	97,32	5,04	82,65	213,41
Ni	0,07	0,01	0,02	11,93	0,06	0,08
Sr	2,66	0,12	0,41	21,50	2,38	2,94
V	0,01	0,00	0,01	2,88	0,00	0,02
Zn	0,87	0,60	1,35	1,44	-0,81	2,54

In the groundwater samples of rainy period: TDS-EC; NH₃-EC; B-NO₃; Cl-EC and TDS; Mg-T.Hard; Na-EC, TDS, NH₃ and Cl; Ni-Co; V-EC, TDS, NH₃, Cl and Na element pairs have very high positive correlation (Table 9). But Ca-NO₃; Cl-T.Alkalinity and B; Co-T, alkalinity; Mg-Ca; Na-B; Sr-NO₃ and B; V-T.Alkalinity element pairs show a high negative correlation.

In the analyses of old periods, uniform distribution maps belonging element pairs of EC-NH₃ and Na-V having very high positive correlation exhibit similar appearances (Figure 6) (Table 9). Nevertheless, each element of Ca-Mg and Cr-Li element pairs in groundwater concentration having moderate negative correlation demonstrates different distributions (Figure 6 and 7). When Figure 6, 7 and 8 were examined, it was determined that element pairs such as Ca-Li, Fe-Na and Ni-V had different concentration

distributions with each other. No correlation with one another was found in correlation analyses of them (Table 9).

Table 9. Correlation coefficients between the element pairs of the water samples of rainy period

	pH	EC	TDS	T Alk.	T Hard.	Turb.	NH3	NO3	SO4	B	Ca	Cl	Co	Cr	Fe	K	Li	Mg	Na	Ni	Sr	V
pH	1,00																					
EC	0,48	1,00																				
TDS	0,40	0,98	1,00																			
T Alk.	-0,13	-0,54	-0,50	1,00																		
T Hard.	0,69	0,73	0,72	-0,30	1,00																	
Turb.	0,69	0,28	0,23	-0,13	0,64	1,00																
NH3	0,42	0,88	0,81	-0,43	0,59	0,28	1,00															
NO3	-0,44	-0,49	-0,50	0,30	-0,13	0,05	-0,20	1,00														
SO4	0,52	0,60	0,61	0,18	0,55	0,09	0,39	-0,57	1,00													
B	-0,58	-0,58	-0,54	0,45	-0,26	-0,26	-0,34	0,91	-0,50	1,00												
Ca	-0,15	-0,13	-0,06	0,03	-0,48	-0,41	-0,39	-0,69	0,11	-0,46	1,00											
Cl	0,40	0,96	0,95	-0,73	0,64	0,28	0,82	-0,51	0,41	-0,62	-0,06	1,00										
Co	-0,20	0,07	0,12	-0,64	-0,15	-0,33	-0,24	-0,45	-0,17	-0,34	0,58	0,25	1,00									
Cr	-0,40	0,21	0,32	-0,14	0,09	-0,44	-0,16	-0,23	0,36	-0,06	0,27	0,20	0,50	1,00								
Fe	0,31	-0,05	-0,01	-0,42	0,20	0,27	-0,39	-0,39	-0,06	-0,40	0,37	0,10	0,70	0,21	1,00							
K	-0,37	-0,13	-0,13	0,29	-0,45	-0,39	-0,15	-0,17	0,24	-0,12	0,41	-0,19	0,09	0,30	-0,27	1,00						
Li	0,37	0,53	0,45	-0,19	0,25	0,48	0,72	-0,16	0,17	-0,39	-0,14	0,51	-0,32	-0,48	-0,36	0,21	1,00					
Mg	0,52	0,79	0,76	-0,32	0,91	0,52	0,81	0,05	0,44	-0,12	-0,66	0,70	-0,31	-0,01	-0,16	-0,40	0,42	1,00				
Na	0,48	0,99	0,95	-0,52	0,66	0,27	0,87	-0,55	0,64	-0,66	-0,08	0,94	0,06	0,19	-0,07	0,00	0,59	0,73	1,00			
Ni	-0,42	-0,07	0,03	-0,28	-0,35	-0,50	-0,43	-0,48	-0,01	-0,29	0,78	0,06	0,86	0,70	0,51	0,40	-0,39	-0,52	-0,04	1,00		
Sr	0,04	0,58	0,62	-0,31	0,20	0,06	0,27	-0,62	0,51	-0,68	0,35	0,60	0,24	0,56	0,10	0,33	0,25	0,15	0,64	0,45	1,00	
V	0,33	0,97	0,95	-0,61	0,61	0,13	0,90	-0,43	0,49	-0,50	-0,15	0,96	0,13	0,22	-0,14	-0,08	0,52	0,75	0,96	-0,03	0,53	1,00

- Very high positive correlation (0.85 to 1.00)
- High positive correlation (0.60 to 0.85)
- Moderate positive correlation (0.45 to 0.60)
- Low positive correlation (0.30 to 0.45)
- No correlation (-0.30 to 0.30)
- Low negative correlation (-0.45 to -0.30)
- Moderate negative correlation (-0.60 to -0.45)
- High negative correlation (-1.00 to -0.60)

Three significant groups appear in the cluster analysis of the groundwater samples of dry period (Figure 11). The first group is named as “Main Component Group” and consists of (EC-TDS-Sr-Mg-Na-NH₃-K-Turb.-T.Hard.-Li)-SO₄. The second group is “Metal Group” and it consists of (Cr-Ni)-Fe. The other group is “Cl Group” and it consists of B-Cl.

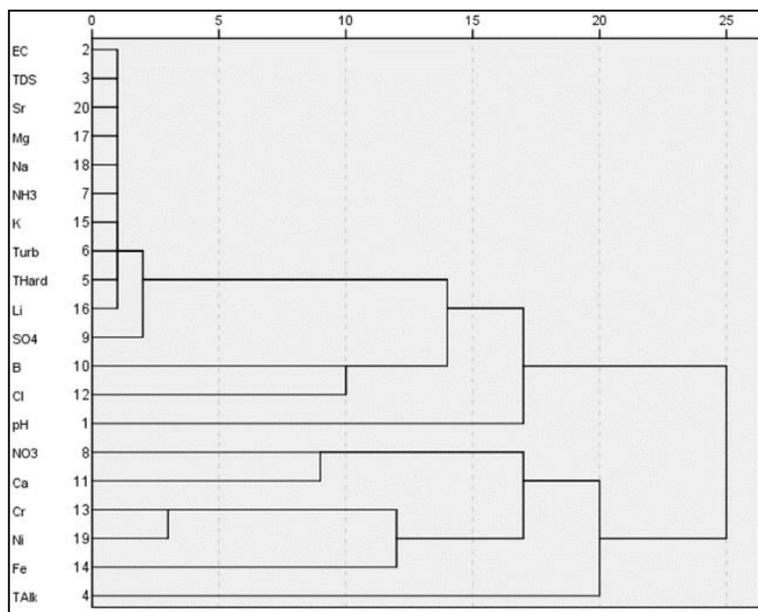


Figure 11. Cluster analysis graphic of the water samples of dry period

Three significant group appears on the cluster analysis of the groundwater samples of rainy period (Figure 12). The first group is named as “Main Component Group” and consists of (EC-TDS-Na-V-Cl)-NH₃-((Mg-T.Hard.)-(pH-Turb))-Sr-SO₄. The Second significant group is named as “Metal Group” and consists of (((CO-Ni)-Ca)-Cr)-Fe)-K. The third group is named as “B Group” and consists of (B-NO₃)-T.Alkalinity.

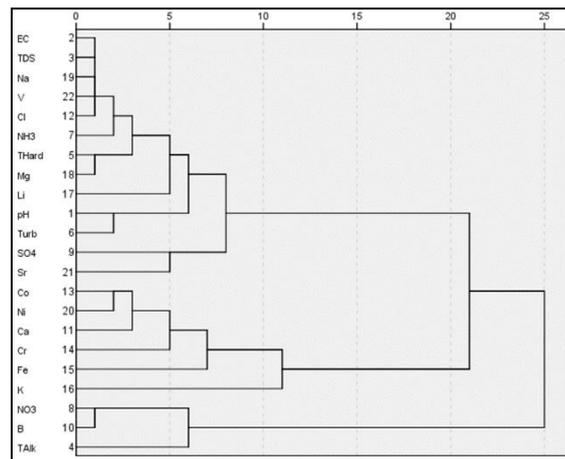


Figure 12. Cluster analysis graphic of the water samples of rainy period

5. Conclusions and Recommendations

The following results were obtained in the study on which the effect of the third OIZ, in which 90% of the factory consists of chemistry, glass, metal and machine production, to the groundwater pollution is based.

According to the concentration distribution maps belonging to both periods, increased levels of EC, Cl, Li, Mg, Mn, Na, V, SO_4 , Sr, Ca, and NH_3 appeared near the east or the north-eastern parts of the study area. Zn appeared to have intensified in the central part, while other elements have increased in other directions. Results also showed that the groundwater has been affected by industrial activities in the OIZ, since Cr, Mg, Fe, and Ni concentrations were found to be high in all samples, while Co, Fe, Li, and Sr concentrations were found in changing amounts. This contamination is mainly due to storage areas and waste belonging to the chemical and metal industries and the factories that produces electrical machines and equipment.

Water samples is usually in the class "mixed compound waters, none of the ions of which exceeds 50%" in both periods according to the Piper diagram when evaluated in terms of water quality. Water samples are mainly classified as "well-usable for irrigation purposes" according to the Wilcox diagram. However, 2 and 10 numbered samples are classified "suspicious-not appropriate", 1 and 11 numbered samples are classified as "not appropriate" during the rainy period.

It was determined that NO_3 , SO_4 , Ca, Cl, Na, Cr, Fe, Mg, Mn, Ni and Zn levels exceeded the MCL in samples according to WHO, EPA and EC drinking water standards. Furthermore, it was established that the water samples of rainy period had higher concentrations than that of dry one. The washing of storage and production areas of factories located in the OIZ in rainy period causes the infiltration of contaminants from the ground to underground. Also due to leakage from the sewage system, an increase in concentration of the elements at the samples taken from groundwater in rainy period when compared with dry period is observed.

In the analyses performed, maximum conductivity values displayed alterations between 4 380 (wet period) and 6 900 (dry period) $\mu\text{mhos cm}^{-1}$. The fact that conductivity values were so high and that, in nearly all samples, Ca and SO_4 concentrations exceeded MCL values indicates that such values are caused by salt and gypsum levels in the aquifer. Parallel to this, Ca, Cl, Na, and SO_4 concentrations were spread such a large area that they suit the boundary of the Aslimyayla formation, which constitutes a natural contamination source for the study area due to its salt and gypsum layers. That NO_3 exceeds MCL in some samples is mainly due to fertilizers used in agricultural activities in the area around the OIZ, reach to irrigation water and groundwater.

In correlation analyses of groundwater samples, it was determined that element pairs in dry and wet seasons had a correlation changing from positive to negative. Of these results, it was found out that very

similar distributions in uniform concentration maps of groundwater of element pairs with high positive correlation were existed. It was determined that there was a very close relationship between statistical results changing from moderate correlation to high correlation and concentration distribution maps.

In cluster analyses of groundwater samples, it is seen that the number of alignment has increased according to dry season graphic in wet season graphic and that the differentiation has become evident. In wet season, there has been witnessed that there has been a decrease in the number of element in "Main Component Group", while there has been an increase in "Metal Group". This crucial differentiation in wet season shows that climatic conditions and changes in chemistry of ground water depending on precipitation increase are very influential.

In cluster analyses of dry season, it has been determined that the elements under "Main Component Group" have encompassed the elements having high concentrations in the analyses of this period. Cluster analysis results prove that water samples are in close relations with the analyses.

According to data from analyses and on site measurements of groundwater samples obtained from wells within the study area, the groundwater of the OIZ is alarmingly contaminated due to rapid industrialization. However, the results of this investigation also suggest that the area's geological properties pose another threat to the area's groundwater. In addition to all these, it is determined that the underground water in the area has a risk in terms of public health.

According to results obtained by this study, the following suggestions should be considered:

Firstly, to prevent contamination stemming from industrial activity, it is necessary that solid and liquid waste be disposed so that they will not infiltrate the groundwater. Secondly, regular groundwater quality monitoring network stations should be established throughout suitable observation wells. Thirdly, there should be sufficient distance between sewage and drinking water supply lines to avoid cross-contamination. Finally, by means of this study, it is well comprehended that it is essential aquifers where the need for drinking water and utilization water can be met should be chosen from the areas which do not pose a threat in terms of public health.

The untreated effluence emerging from industries in Konya's third OIZ must be monitored in order to maintain the standards prescribed by the pollution control board for various industries in the region. At the same time, to prevent contamination that can stem from lithology, it is necessary that wells drilled in the area be planned so that they can be isolated from salt and gypsum deposits.

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