JOURNAL OF SCIENCE
SAKARYA UNIVERSITY

Sakarya University Journal of Science

ISSN 1301-4048 | e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University | http://www.saujs.sakarya.edu.tr/en/

Title: Groundwater Pollution Connected to Multiple Effect: A Case Study Kaman (Kırşehir, Turkey)

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Recieved: 2019-04-15 19:37:20

Accepted: 2020-07-27 22:28:21

Article Type: Research Article
Volume: 24
Issue: 5
Month: October
Year: 2020
Pages: 1008-1022

How to cite
Tülay EKEMEN KESKİN, Bahadır SUBAŞI, Feyza GİRİŞEN, Zeynel BAŞIBÜYÜK; (2020), Groundwater Pollution Connected to Multiple Effect: A Case Study Kaman (Kırşehir, Turkey). Sakarya University Journal of Science, 24(5), 1008-1022, DOI: https://doi.org/10.16984/saufenbilder.554148
Access link
http://www.saujs.sakarya.edu.tr/en/pub/issue/56422/554148

JOURNAL of SCIENCE
Sakarya University
Journal of Science
VOLUME: 24
ISSUE: 5
OCTOBER 2020

Sakarya University Journal of Science 24(5), 1008-1022, 2020

SAKARYA UNIVERSITY

Groundwater Pollution Connected to Multiple Effect: A Case Study Kaman (Kırşehir, Turkey)

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Abstract

This study aim to detect the groundwater pollution connected to multiple effect such as the interaction of mineral/ore-water, mining destruction and agricultural activities in Kaman (Kırçehir). The study area has recently abondoned iron, antimony, gold and floride mine areas and so, there are a lot of mine piles. Mine waste is a rich source of hazardous trace elements to the environment. In many areas expecially abandoned sulphidic mine wastes may cause to produce acid mine drainage. Although no acid mine drainage is observed in the study area, the region needs to be reworked for this purpose in the following years. The electrical conductivity, pH and Eh values of the waters range between 126-1994 µS/cm; 7.28-8.58; 222-649 mV respectively. In the rainy season, the pH values of the waters decreased due to the effect of slight acidic precipitation and in parallel with this decrease, EC, TDS, Ca, Na, SO_4, HCO_3, As, Sb, U concentrations of some waters increase due to the increase of solubility of elements. As, Sb, F, U, NO_3, NH_4 concentrations some of water exceed the maximum limit values given in the Turkish and World Health Organization Standards. Especially As contamination is a big problem for the region, because of tens of times exceed drinking water regulations.

Keywords: Groundwater pollution, mineral-water interaction, mining destruction, agricultural activities, Kaman (Kırşehir)

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1. INTRODUCTION

The diminished water resources due to the overuse, the contamination of surface and groundwater, and decline of the rainfall etc. is very big problem for the many region of the World. Especially in recent years, the water and soil are exposed the contamination due to the agricultural, mining and industrial activities and their wastes, geothermal water wastes, and rapid population growth. Therefore, many researchers focused on water and soil pollution studies to protect the environment. There are numerous groundwater pollution problems in Turkey associated with geogenic and/or anthropogenic pollution sources [1-5]. Geogenic factors occur as important as anthropogenic pollution sources affecting the quality of groundwater. Anthropogenic pollution sources such as mining and agricultural activities increases the negative effects of lithology on groundwater quality [1, 3, 6]. Turkey hosts numerous active and abandoned mine areas that are characterized by metal–rich water [2, 4]. Figure 1 show the study region that is located north of Kırsehir (Central Anatolia Region of Turkey). This study purposes at elucidating the groundwater pollution resulting from water–rock interaction, mining and agricultural activities and mine tailings at the study area and especially, it is aimed to assign the origin of trace element impurities in water. For this aim, insitu physical measurements were made, and for chemical and isotopical analysis groundwater samples were taken, and As, Sb, F, U, NO_3, NH_4 element pollution was observed in groundwater. Pollutant levels were especially higher in groundwaters from discharging Kızılırmak and Meşeköy formations consisting of clastic rocks and magmatic rocks consisting of Fe, Sb, Au and F ores.

Many toxic contaminants and heavy metals can originate from many natural and anthropogenic pollutant sources. While agricultural, mining and indusrtial activities are anthropogenic, rock weathering and thermal environment compose natural or geological sources [8]. Many of trace elements such as As, Sb, Pb etc. are one of the most serious nature contaminants due to high toxicity [7]. Arsenic cause discomfort of many organ systems. Furthermore, it is determined that, chronic arsenic exposure is related to bladder, kidney, skin, and liver cancers. Also it is know that inorganic arsenic is more harmfull than organic arsenic [9-11].

2. MATERIAL AND METHODS

The study was performed between June 2016 and May 2017. The EC (Electrical conductivity), TDS (Total Dissolved Solids), T (Temperature), pH, ORP, and Q (Discharge) were measured on site with multiparameter (YSI-256 Instrument) of the 42 water samples (28 springs, 13 wells and 1 surfacewater) in the study region. Polyethylene bottles were prefered for the chemical and isotopic analysis of water. The pH meter was calibrated against to pH 4, 7, and 10 buffer solutions. The Oxidation Reduction Potential (ORP) measurements were conducted using a platinum electrode calibrated with a zobell reference. The ORP values were converted to the Eh by adding aproximately 200 mV as specified by the YSI-256 instrument catalog. Acidification to pH < 2.0 for trace element analysis was made using pure nitric acid. The high–performance ion chromatography system (HPIC) and inductively coupled plasma–mass spectroscopy (ICP–MS) at Hacettepe University were used for major ion and trace element analyses, respectively. Tritium and oxygen-18-deuterium isotopes analyses were carried out at the Environmental Tritium Laboratory and International Karst Water Resources Application and Research Center of the Geological Engineering Department Hacettepe University, respectively.

3. GEOLOGICAL BACKGROUND and HYDROGEOLOGY

The base rocks of the study area are Paleozic aged Kırşehir massive (Kalkanlıdağ, Kervansaraydağ, Bozcaldağ and Hacıselimli Formation) consisting of massive, gnays, green schist, marble, amfibolite and metagabbro with magmatic origin. Massif in metamorphic rocks tectonically covered by the Çiçekdağ Formation which consists of volcanic rocks intercalated Cenomanian-Santonian aged pelagic sediments. These units are overlain by Campanian-Maestrichian aged intrusions named Baranadağ

Granitoid and Buzlukdağ Siyenitoid which show large expansions in the region. Another unit occupying a large area in the study area is defined as Kızılırmak Formation, which contains layerless, blocky, conglomerate, sandstone, limestone, tuff, gypsum and mudstones and defined as Meşeköy Formations, which contains conglomerate, sandstone, mudstone with limestone [12-14] (Figure 2). The floride mineralization in the Bayındır region has developed as vein type ores and is located within the fractures/cracks of Buzlukdağ Siyenitoide [15]. The reason for magnetite mineralization in Durmuşlu and Büğüz regions are the rise during orogenic activity of Paleozoic aged marbles and the mix of this marble when after a long period of wear with basic magma blocks in the Upper Cretaceous. Briefly, ores have generally developed due to orogenic activity and subsequent acid intrusions [16].

The main aquifers in the study area are conglomeratic and sandy levels of Kızılırmak Formation and Meşeköy Formations; the Baranadağ Granitoyid consisting of granites and the Buzlukdağ Siyenitoyid consisting of syenites. While the conglomerate and sandstone show grained aquifer properties, granites and syenites show fractured-cracked aquifer properties. Kervansaraydağ Formation with quartzite, schist, marble strips and Bozçaldağ Formation consisting of marble show aquiferous features in fracture-cracked levels in some places. All of these springs and wells measured in the study region are used as drinking, domestic and/or irrigation aims. The geological-hydrogeological map which included water sampling points are given in the Figure 2.

Table 1 show physicial and chemical properties of waters. 10 springs discharges from the Kızılırmak Formation with flow rates between 0.15 and 3.32 L/s. There are also 6 wells drilled in the formation. There are 3 springs and 6 wells discharging from the Meşeköy Formation. 4 springs discharges from Baranadağ Granitoyid with flow rates between 0.23 and 2.97 L/s. There are 4 springs with flow rates between 0.035 and 0.4 L/s discharging from the Buzlukdağ Siyenitoyid. 1 spring was observed in the Kervansaraydağ Formation and there are 5 springs discharging from the contact of Baranadağ Granitoyid and Kervansaraydağ Formations.

4. WATER CHEMISTRY AND POLLUTION

There are different geological units, generellay abandoned iron, gold, antimony and floride mine area and mining and agricultural activity in the study region. Therefore groundwater show large differences due to physical and chemical properties and the groundwaters are contaminated with depending As, Sb, F, U, NO_3 and NH_4.

Electrical conductivity (EC) and pH values of waters (KM-K1, KM-K3, KM-K4, KM-K5, KM-K6, KM-K7, KM-K8, KM-K9, KM-K10, KM-K13, KM-G9, KM-G10, KM-G12, KM-G13, KM-G14, KM-G16, KM-G18) discharging from Kızılırmak Formation consisting of clastic levels with block are between 352 and 963 µS/cm; and 7.28 and 8.15, respectively. EC and pH values of waters (KM-G1, KM-G2, KM-G3, KM-G4, KM-G5, KM-G6, KM-G7, KM-G8, KM-G19) discharging from Meşeköy Formation formed of clastics are between 430 and 781 µS/cm; and 7.29 and 8.70, respectively. It is thought that the variation in EC values of spring discharging from these formation is due to different groundwater residence times. Furthermore, the various rock types, such as conglomerate, sandstone, mudstone have different dissolution and permeability value. EC and pH values of waters (KM-K12, KM-K18, KM-G15) discharging from Baranadağ Granitoide are between 126 and 314 µS/cm; and 7.92 and 8.53, respectively. EC and pH values of waters (KM-K14, KM-K15, KM-K17) discharging from Buzlukdağ Syenitoide are between 268 and 516 µS/cm; and 7.36 and 8.05, respectively. It is thought that the EC values of waters discharging from magmatic rocks such as granite and syenite, especially around ore deposits, may have been affected by the mineralizations found in these rocks and the destruction during the mining activities.

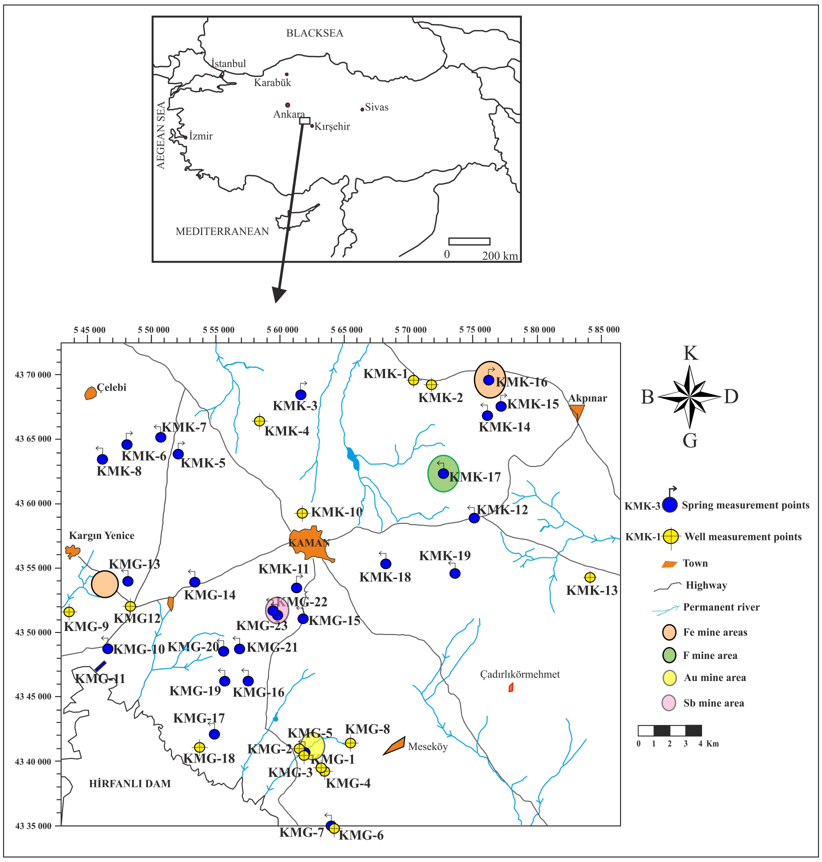

Figure 1 Location of the study area and its vicinity

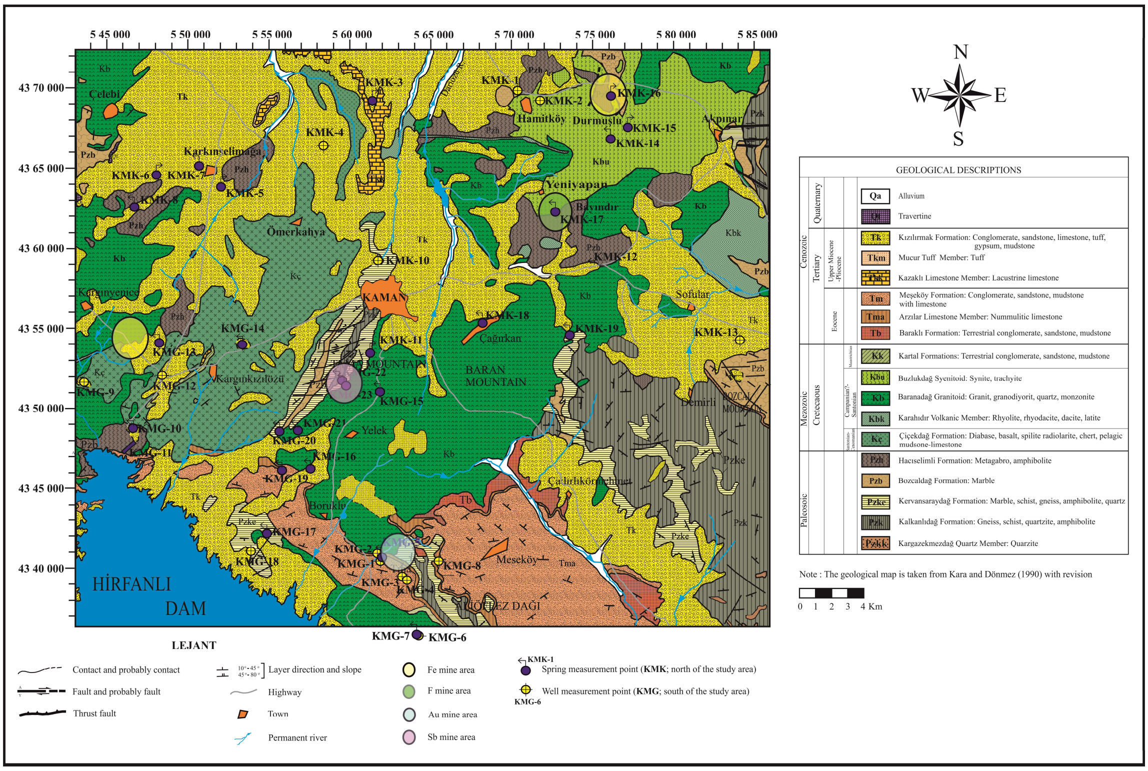

Figure 2 Geological-hydrogeology map of the study area and its vicinity (The geological maps are taken from Kara and Dönmez (1990) [10] with revision

Table 1

Field measurement datas and chemical analysis results (meq/l) of the groundwaters in the study area and Turkish Standards for Water Intended for Human Consumption (EC (µS/cm), TDS (mg/L), Eh (mV), Temperature (ºC))

No	Date	EC	TDS	pH	Eh	Temp.	Na^+	K^+	Mg^{++}	Ca^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	NH_4^+	NO_2^-	NO_3^-	F^-	As	Sb	U
KM-K1	28.06.2016	499	325	8.15	275	18.58	0.94	0.05	1.75	3.14	0.00	4.71	0.25	0.46	**0.11**	0.00	0.38	0.05	5.5	0.33	9.6
KM-K2	28.06.2016	461	299	8.11	283	19.71	0.72	0.02	1.87	3.08	0.00	4.41	0.18	0.41	**0.05**	0.00	0.24	**0.08**	2.4	0.08	**17.5**
“	03.05.2017	494	321	7.64	326	12.65	0.39	0.01	0.86	3.17	0.00	4.37	0.07	0.23	0.00	0.00	0.15	0.03	1.90	0.07	**16.48**
KM-K3	28.06.2016	731	475	8.04	292	20.78	3.30	0.03	2.12	3.36	0.59	5.10	0.98	0.27	**0.04**	0.00	1.17	0.06	**11.7**	0.04	8.0
“	03.05.2017	786	511	7.28	354	13.65	1.80	0.01	1.00	3.56	0.00	5.73	0.46	0.15	0.00	0.00	0.57	0.02	**10.36**	0.08	7.32
KM-K4	28.06.2016	481	313	8.15	302	19.98	0.52	0.01	1.84	3.35	0.00	4.12	0.12	0.23	0.02	0.00	**0.91**	0.03	0.4	0.03	2.4
“	03.05.2017	515	335	7.62	347	13.52	0.46	0.01	1.24	3.91	0.00	3.88	0.09	0.27	0.00	0.00	**0.88**	0.03	0.33	0.02	2.30
KM-K5	28.06.2016	613	399	8.02	649	17.55	1.24	0.02	2.75	3.51	0.00	5.88	0.30	0.40	**0.04**	0.00	0.48	0.03	**24.6**	0.17	5.4
“	03.05.2017	637	414	7.75	344	12.20	1.30	0.00	1.78	4.32	0.00	5.73	0.28	0.49	0.00	0.00	0.40	0.02	**21.53**	0.15	4.78
KM-K6	28.06.2016	488	317	8.14	367	17.34	0.63	0.02	1.86	3.42	0.00	4.71	0.12	0.28	**0.04**	0.00	0.46	0.02	**23.4**	0.34	2.9
“	03.05.2017	512	333	7.62	347	11.58	0.57	0.01	1.07	4.11	0.00	4.37	0.13	0.31	0.00	0.00	0.42	0.03	**20.32**	0.31	2.67
KM-K7	28.06.2016	469	305	8.04	352	14.14	0.82	0.02	2.09	3.05	0.59	4.12	0.13	0.21	**0.03**	0.00	0.43	0.02	**19.4**	0.20	2.5
“	03.05.2017	503	327	7.56	356	11.65	0.86	0.00	1.46	3.74	0.00	4.76	0.09	0.23	0.00	0.00	0.43	0.04	**18.13**	0.28	2.47
KM-K8	28.06.2016	529	344	7.94	334	14.13	0.87	0.04	2.43	3.35	0.00	5.20	0.27	0.30	**0.07**	0.00	0.37	0.04	**12.7**	0.17	4.7
“	03.05.2017	568	369	7.53	361	12.91	0.91	0.03	1.50	4.04	0.00	4.95	0.21	0.35	0.00	0.00	0.40	0.02	**16.22**	0.17	4.99
KM-K10	29.06.2016	624	406	7.65	313	16.01	0.66	0.07	1.34	5.52	0.00	4.90	0.69	0.86	**0.07**	0.00	0.63	0.00	7.9	0.25	0.7
“	04.05.2017	711	462	7.30	348	16.19	0.63	0.09	1.06	6.28	0.00	5.24	0.76	1.05	0.00	0.00	0.68	0.00	9.03	0.24	1.50
KM-K11	29.06.2016	390	253	8.07	295	14.39	0.14	0.01	0.44	3.32	0.00	3.31	0.08	0.20	0.01	0.00	0.11	0.00	1.1	0.18	2.6
KM-K12	29.06.2016	314	204	7.92	301	13.85	0.42	0.02	1.08	2.42	0.00	2.94	0.07	0.29	0.01	0.00	0.43	0.02	1.3	0.04	3.3
KM-K13	29.06.2016	352	229	7.91	300	22.03	0.10	0.01	1.02	3.08	0.00	3.82	0.05	0.07	0.01	0.00	0.25	0.00	0.7	0.03	0.6
KM-K14	29.06.2016	457	297	8.05	257	14.15	0.93	0.02	1.59	3.36	0.00	5.10	0.11	0.31	0.01	0.00	0.01	0.07	6.8	0.20	14.9
KM-K15	30.06.2016	268	174	7.87	282	16.23	0.81	0.02	0.69	2.03	0.00	2.94	0.07	0.18	0.01	0.00	0.01	**0.10**	2.3	0.14	13.1
“	03.05.2017	289	185	7.53	339	11.55	0.83	0.02	0.50	2.02	0.00	2.72	0.08	0.23	0.00	0.00	0.01	**0.10**	2.03	0.10	9.56
KM-K16	30.06.2016	459	298	7.8	279	16.51	0.83	0.02	2.03	3.03	0.00	4.80	0.10	0.47	**0.03**	0.00	0.19	0.05	2.0	0.18	**20.7**
“	03.05.2017	500	325	7.65	317	12.91	0.86	0.02	1.27	3.82	0.00	4.66	0.08	0.62	0.00	0.00	0.21	0.05	1.77	0.06	**19.95**
KM-K17	30.06.2016	491	319	7.86	272	14.76	0.82	0.02	1.88	3.49	0.00	4.61	0.28	0.52	0.02	0.00	0.17	**0.18**	**10.5**	0.28	**36.9**
“	03.05.2017	516	335	7.36	354	13.75	0.85	0.01	1.35	4.13	0.00	4.76	0.25	0.58	0.00	0.00	0.17	**0.17**	9.39	0.26	**33.69**
KM-K18	30.06.2016	199	131	8.03	275	15.42	0.37	0.01	0.59	1.74	0.00	2.16	0.06	0.29	0.01	0.00	0.01	0.01	**27.4**	0.06	2.3
“	03.05.2017	229	149	7.92	333	11.19	0.40	0.01	0.46	2.04	0.00	2.04	0.08	0.56	0.00	0.00	0.01	0.01	**23.94**	0.06	1.44
KM-K19	30.06.2016	299	135	7.87	277	15.95	0.27	0.03	0.77	2.90	0.00	3.33	0.06	0.18	0.01	0.00	0.07	0.01	**23.9**	0.06	1.2
“	03.05.2017	233	151	7.61	350	11.97	0.37	0.02	0.44	2.03	0.00	2.14	0.05	0.36	0.00	0.00	0.04	0.02	2.85	0.03	0.90
Sağ. Bak. (2013)															**0.03**		**0.81**	**0.08**	**10**	**5**	

Table 1 Continue

No	Date	EC	TDS	PH	Eh	Temp.	Na^+	K^+	Mg^{++}	Ca^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	NH_4^+	NO_2^-	NO_3^-	F^-	As	Sb	U
KM-G1	27.06.2016	549	357	8.58	221.7	16.39	0.78	0.08	1.67	4.17	0.00	4.80	0.38	0.89	0.00	0.03	0.14	0.02	**69.3**	0.97	1.6
"	04.05.2017	595	386	7.29	320.6	15.35	0.45	0.04	0.78	3.85	0.00	4.85	0.18	0.51	0.00	0.00	0.06	0.03	**87.36**	1.07	2.71
KM-G2	27.06.2015	439	285	8.32	238.6	19.23	0.49	0.05	1.21	3.66	0.00	4.31	0.25	0.42	0.00	0.03	0.14	0.01	**398.4**	0.32	3,0
KM-G3	27.06.2016	497	323	8.23	257.5	22.35	0.74	0.04	2.00	3.07	0.00	4.02	0.34	0.87	0.00	0.02	0.23	0.01	**16.2**	0.78	2.0
KM-G4	27.06.2016	502	326	8.15	255.9	15.24	0.58	0.04	1.82	3.80	0.00	4.22	0.29	0.87	0.00	0.02	0.32	0.01	**23.1**	0.95	1.2
KM-G5	27.06.2016	430	280	8.70	256.5	21.75	0.62	0.04	1.03	3.48	0.00	3.92	0.26	0.43	0.00	0.02	0.15	0.01	**221.5**	0.27	1.1
"	04.05.2017	506	331	7.43	283.9	16.49	0.33	0.02	0.67	3.54	0.00	4.37	0.16	0.35	0.00	0.00	0.11	0.00	**256.69**	0.42	2.62
KM-G6	27.06.2016	453	316	8.14	257.5	21.43	0.87	0.05	1.70	3.12	0.00	4.12	0.42	0.38	0.00	0.02	0.46	0.03	**30.7**	0.75	4.6
"	04.05.2017	504	328	7.46	334.4	15.74	0.45	0.02	0.83	3.25	0.00	4.27	0.20	0.22	0.00	0.00	0.18	0.04	**37.69**	0.74	4.39
KM-G7	27.06.2017	510	332	8.01	259.2	19.84	1.85	0.04	1.56	2.29	0.00	4.02	0.47	0.49	0.00	0.05	0.32	0.06	**43.3**	0.12	15.0
"	04.05.2017	550	358	7.35	335	13.64	1.06	0.02	0.91	2.83	0.00	4.47	0.26	0.31	0.00	0.00	0.17	0.06	**38.53**	0.13	14.05
KM-G8	27.06.2017	781	512	7.92	255.7	14.38	0.74	0.04	2.19	6.39	0.00	4.61	1.71	0.68	0.00	0.03	**1.76**	0.01	**54.2**	0.16	0.9
"	04.05.2017	511	332	7.38	308.2	14.45	0.29	0.02	0.64	3.70	0.00	4.27	0.17	0.21	0.00	0.00	0.21	0.00	**68.10**	0.20	2.18
KM-G9	28.06.2016	856	556	8.03	319.6	15.90	4.01	0.12	3.41	3.40	0.78	4.02	0.68	3.52	0.00	0.02	**1.04**	0.13	**9.8**	0.11	8.5
"	04.05.2017	963	626	7.76	318.5	13.45	1.86	0.07	1.81	3.40	0.00	4.56	0.40	2.27	0.00	0.00	0.49	0.05	8.48	0.13	7.98
KM-G10	28.06.2016	801	521	8.08	494.4	24.19	4.16	0.03	2.16	3.19	0.98	4.31	1.43	1.48	0.00	0.05	0.67	0.05	0.6	0.03	5.3
KM-G11	28.06.2016	1994	1296	8.05	372.2	16.22	6.62	0.16	4.27	8.57	0.00	2.95	7.47	7.39	0.01	0.04	0.01	0.01	**11.2**	0.31	2.0
KM-G12	28.06.2016	586	381	8.11	321.4	13.88	1.08	0.02	1.89	3.31	0.00	4.92	0.20	0.37	0.00	0.02	0.29	0.03	0.8	0.06	3.7
KM-G13	28.06.2016	516	335	8.01	322.4	14.67	0.99	0.08	1.97	3.17	0.59	4.02	0.15	0.41	0.00	0.02	0.50	0.03	**14.4**	0.10	4.1
"	04.05.2017	567	369	7.75	319.7	13.45	0.45	0.02	1.05	3.53	0.00	4.85	0.09	0.18	0.00	0.00	0.34	0.04	1.68	0.07	1.71
KM-G14	28.06.2016	502	326	8.09	323.8	18.32	0.68	0.01	2.18	3.35	0.39	4.31	0.10	0.27	0.00	0.01	0.64	0.02	0.6	0.04	1.6
KM-G15	29.06.2016	126	82	8.53	289.3	14.18	0.30	0.01	0.57	1.42	0.00	1.26	0.27	0.15	0.00	0.01	0.41	0.01	0.3	0.03	0.1
KM-G16	29.06.2016	508	330	8,07	307.2	18.63	0.53	0.02	1.50	4.14	0.00	4.90	0.13	0.34	0.00	0.03	0.46	0.03	2.8	0.11	5.3
KM-G17	29.06.2016	339	221	8.15	313.2	16.09	0.27	0.02	0.90	2.74	0.00	2.94	0.20	0.30	0.00	0.01	0.19	0.01	6.2	0.03	0.7
KM-G18	29.06.2016	826	537	7.99	311.7	19.48	2.17	0.04	2.60	5.06	0.00	4.22	1.77	1.31	0.00	0.03	**1.78**	0.03	**14.0**	0.04	10.3
"	04.05.2017	875	569	7.46	329.9	15.88	1.07	0.02	1.16	4.48	0.00	4.27	0.85	0.74	0.00	0.00	0.77	0.01	**15.37**	0.06	11.06
KM-G19	29.06.2016	465	302	8.17	314.4	23.56	0.36	0.02	1.48	3.84	0.00	4.31	0.17	0.38	0.00	0.01	0.47	0.01	2.5	0.09	3.1
KM-G20	29.06.2016	335	218	8.05	308.2	15.42	0.17	0.01	1.12	3.01	0.00	3.53	0.08	0.23	0.00	0.01	0.12	0.00	2.7	0.03	0.3
KM-G21	29.06.2016	318	207	8.17	305.7	18.57	0.09	0.01	0.36	3.53	0.00	3.53	0.06	0.16	0.00	0.01	0.06	0.00	**20.5**	0.04	0.5
KM-G22	29.06.2016	361	234	7.94	309.1	13.15	0.21	0.03	0.72	3.45	0.00	3.73	0.08	0.22	0.00	0.01	0.17	0.01	**119.6**	**11.03**	1.2
"	04.05.2017	389	253	7.59	346.4	11.37	0.15	0.01	0.37	3.45	0.00	3.88	0.04	0.15	0.00	0.00	0.09	0.01	**148.61**	**12.66**	2.74
KM-G23	29.06.2016	286	186	7.86	310.5	15.5	0.14	0.04	0.39	3.08	0.00	3.24	0.06	0.14	0.00	0.01	0.05	0.00	**11.7**	1.27	4.1

Electrical conductivity (EC) and pH values of waters (KM-G17, KM-G20, KM-G21, KM-G22, KM-G23) discharging from contact of Baranadağ Granitoyid and Kervansaraydağ Formations consisting of quartzite, schist, marble are between 286 and 389 µS/cm; and 7.59 and 8.17, respectively.

In the rainy season (April-May), the discharge of waters have increased slightly. In parallel with this situation, the pH values have fallen due to the effect of the slightly acidic rain water. This decline led to an increase in the EC, TDS, Ca, Na, SO_4 and HCO_3 values of many waters. It is believed that the reason for these increases is the increase in the solubility of ore deposits and associated rocks in the study area due to this precipitation water.

During the dissolution of the altered rocks, ores and mine piles, some elements were free by hydrolysis along various flowways. Furthermore, it is thought that mining activities and abondoned mine areas accelerated dissolution. In addition that in most region in the world waters were polluted due to chemicals used in agricultural activities. Because the use of fertilizers and pesticides increase for enhance productivity. According to many studies, some major ions, nitrogen pollutants, and trace elements were found in fertilizers and pesticides [17-19, 1].

The NH_4 values of waters range between 0.09 and 1.99 mg/L, and the NH_4 values of the water (KM-K1, KM-K2, KM-K3, KM-K5, KM-K6, KM-K7, KM-K8, KM-K10, KM-G1, KM-G2, KM-G7, KM-G8, KM-G10, KM-G11, KM-G18) discharging from the Kızılırmak and Meşeköy formations (excluding KM-G11), which consists of clastic units, are several times higher than the 0.5 mg/L value given in Turkish Drinking Water Standards [20]. KM-G11 is a water that represents the dam water and is used for domestic purposes after passing through rough grate. Agricultural activities are performed in these regions, and the waters discharging from these lithologies are generally used as drinking, domestic and irrigation water purposes. It is thought that the KM-K10 well is particularly important, because of providing the drinking water of the Kaman District. Similarly, the NO_3 values of waters range between 0.68 and 109.04 mg/L, and the NO_3 values of the water (KM-K3, KM-K4, KM-K10, KM-G8, KM-G9, KM-G18) discharging from the Kızılırmak and Meşeköy formation are several times higher than the 50 mg/L value given in Turkish Drinking Water Standards and World Health Organization standards [21]. Nitrate generally finds in waters organically and anthropogenically. The high nitrate concentrations in the drinking water can cause the ‘‘blue disease’’in babies because of decreases the oxygen carrying capacity of the blood [22]. In addition WHO (1984) [22] and Uslu and Türkman (1987) [23] said that, nitrate may readily converted to nitrite at body part where acidity is relatively low, and nitrite may have strong carcinogenic effects.

The trace elements concentration in water samples are given in Table 1. The As, Sb, F and U amount of waters range between 0.3 and 398.4 ppb (µg/L); 0.03 and 11.66 ppb (µg/L); < 0.01 and 3.35 mg/L; 0.01 and 36.9 µg/L, respectively. Trace element pollutants (As, Sb, F, U) are observed in water (spring and well; KM-K2, KM-K3, KM-K5, KM-K6, KM-K7, KM-K8, KM-K9, KM-K10, KM-K15, KM-K16, KM-K17, KM-K18, KM-K19, KM-G1, KM-G2, KM-G3, KM-G4, KM-G5, KM-G6, KM-G7, KM-G8, KM-G9, KM-G11, KM-G13, KM-G18, KM-G21, KM-G22, KM-G23) discharging from the Kızılırmak and Meşeköy formations consisting of clastics and magmatic (Baranadağ Granitoide and Buzlukdağ Siynenitoide) rocks, and contact with metamorphic of magmatic rocks (Kervansaraydağ/Hacıselimli formations) consisting of Fe, Sb, Au and F mine veins.

Arsenic pollution can be seen in two forms as natural and anthropological. For example, high arsenic contents can also be seen in Pliocene sediments, mining sites, volcanic/magmatic rocks, lakes, and black shales [24-25]. Geological structure is very important in the amount of arsenic originating from natural sources in soils and water. The average arsenic value detectabled on the continental crust varies from 1.5 to 2 ppm [26]. Arsenic can be determined in quartz, feldspar, aluminosilicates and iron ore minerals and the feldspar found in magmatic rocks probably accounts for more than half of total arsenic [27]. Due to this information, it is thought that the sources of pollution in the KM-K17, KM-G1, KM-G2, KM-G5, KM-G22 waters discharging from magmatic and methamorphic rocks near the abandoned iron, anthimony, gold and floride mine and the KM-K18 Spring discharging from Baranadağ Granitoide are the natural washings from the magmatic rocks and mineralizations. However, it is believed that the mining process accelerates the dissolution of trace elements from the rocks and may causes a higher amount of trace elements in the water.

Arsenic amount are is correlated with the ammonium concentrations, which is formed decay the of organic matter. The equations given below proves that there may be a relationship between the input of As into the groundwater and the decay of organic product (Eq. 1, 2, 3) [28-30, 11].

$$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_4^{-} + 3H^{+} + 2e^{-} \quad (1)$$
$$H_3AsO_3 + H_2O \leftrightarrow HAsO_4^{-} + 4H^{+} + 2e^{-} \quad (2)$$
$$CH_4 + 3H_2O \leftrightarrow HCO_{3-} + 9H^{+} + 8e^{-} \quad (3)$$

In addition that, it is also thought that there are two causes of As pollution in other waters which are discharging from Kızılırmak and Meşeköy formation consisting of clastic levels that have carried out agricultural activities. The source rocks of the clastic levels are magmatic and metamorphic rocks in the upper elevations. The first of these reasons is the water-rock interaction, ie naturally washing of the rocks, and the second one is the anthropological pollution due to agricultural activities. Pesticides, drying agents and feed additives that are used for agricultural productivity are amoung the wide use areas of arsenic [26, 27, 31]. This idea is reinforced by a positive association between concentrations of As and NH_4 in the waters. Long-term consumption of arsenic can cause various discomforts in the body. Arsenic accumulated in skin, hair and nails causes color changes in the hands and feet, and can lead to a disease called skin cancer and black foot (blackfoot) in the progressive stages [32-36]. In addition, many studies have indicated that it can cause problems such as respiration, kidney, stomach, heart disorders, blood disorders, diabetes, growth problems in children and intelligence [37-38].

It is believed that the Sb (KM-G22), F (KM-K9, KM-K15, KM-K17, KM-G9), and U (KM-K2, KM-K9, KM-K14, KM-K16, KM-K17, KM-G7) pollutions observed in this waters is due to the water-rock interaction and mining activities. Antimony negatively affect the nerve, respiratory and digestive systems and cause collapse in the immune system [39-40]. Fluoride consumption can often cause discomfort in the teeth and disrupt bone structure in the skeletal system [41]. In addition to long term and high amount of uranium consumption causes kidney disorders and, because it is a radioactive element, it can carry cancer risk [42].

The Piper diagrams [43] that show major anion and cation percentages of the waters in the study region are given Figure 3. Generally, while groundwater have Ca-HCO_3 facies, KM-K3, KM-K5, KM-G7, KM-G9, KM-G10, KM-G11 discharging from Kızılırmak and Meşeköy formation have mix type (Na-Ca-Mg facies). In addition that, KM-G9 and KM-G11 has HCO_3SO_4 and SO_4ClHCO_3 type according to anion respectivelly. KM-G11 is dam water. No changes were made during the rainy (April-May) season. It is thought that the Na-Ca-Mg-HCO_3 type were mostly according to different clastic levels with different originally level such as conglomerate, sandstone, mudstone and locally clayey limestone, tuff, gypsum, anhydrite and ion exchange reactions between water and clastic rocks.

5. ISOTOPE CHEMISTRY

The ^{18}O, ^{2}H, and tritium (^{3}H) isotopes were analysed because of determine the origins and underground residence time of groundwater. The ^{18}O, ^{2}H, are stable isotopes; and tritium (^{3}H) is a radioactive isotope. The results of waters with the large discharge and around the ore deposits according to study aim are given in Table 2.

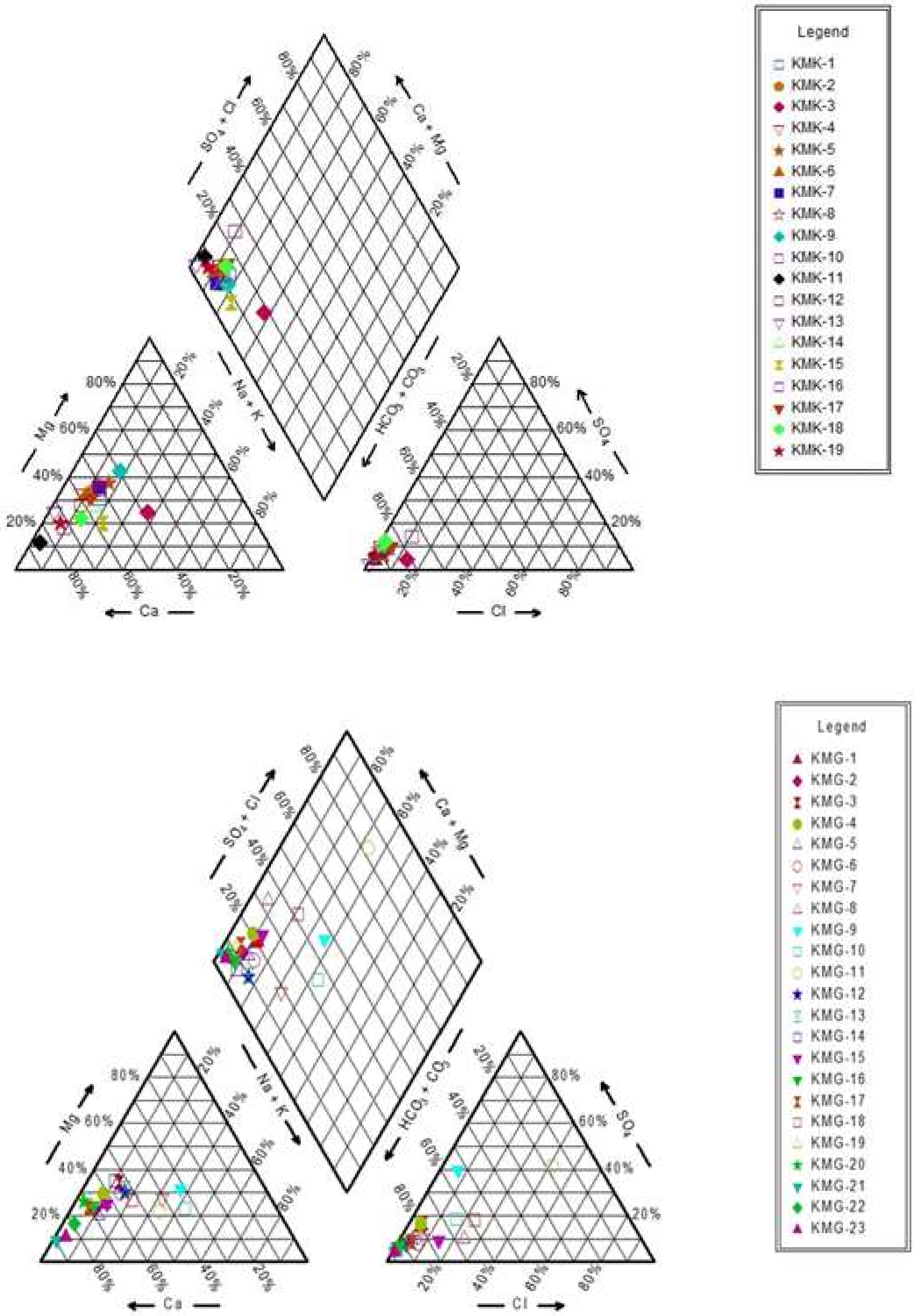

Figure 3 Piper diagram of the groundwaters in the study area (dry period)

Table 2
Isotope analysis results some groundwater in the study area

No	Date	Tritium (TU)	Oxygen-18 (VSMOW ‰) (±0.15)	Deuterium (VSMOW ‰) (± 2)
KM-K8	28.06.2016	3.02 ± 0.28	-8.49 ± 0.20	-63.41 ± 1.49
KM-K10	29.06.2016	3.09 ± 0.28	-10.31 ± 0.05	-71.10 ± 0.57
KM-K13	29.06.2016	2.11 ± 0.26	-10.12 ± 0.15	-70.16 ± 1.23
KM-K15	30.06.2016	3.92 ± 0.29	-10.74 ± 0.21	-72.92 ± 1.04
“	03.05.2017	3.39 ± 0.30	(-)	(-)
KM-K16	30.06.2016	4.45 ± 0.30	-9.81 ± 0.05	-69.31 ± 0.61
KM-K17	30.06.2016	2.99 ± 0.29	-10.33 ± 0.30	-74.28 ± 1.90
“	03.05.2017	3.87 ± 0.32	(-)	(-)
KM-K18	30.06.2016	3.69 ± 0.30	-10.13 ± 0.04	-71.02 ± 0.55
KM-G1	27.06.2016	3.25 ± 0.31	-9.80 ± 0.08	-70.79 ± 0.30
KM-G4	27.06.2016	3.34 ± 0.32	-10.30 ± 0.10	-72.73 ± 0.71
KM-G5	27.06.2016	3.14 ± 0.30	-10.09 ± 0.06	-69.69 ± 0.69
“	04.05.2017	3.04 ± 0.29	(-)	(-)
KM-G8	27.06.2016	3.20 ± 0.30	-9.99 ± 0.25	-68.20 ± 1.52
KM-G11	29.06.2016	3.68 ± 0.30	-6.89 ± 0.14	-51.65 ± 1.82
KM-G13	29.06.2016	3.71 ± 0.30	-9.47 ± 0.08	-66.55 ± 0.76
KM-G15	29.06.2016	3.34 ± 0.30	-10.81 ± 0.27	-68.27 ± 0.82
KM-G20	29.06.2016	3.92 ± 0.30	-10.66 ± 0.03	-71.59 ± 0.56
KM-G22	29.06.2016	3.33 ± 0.31	-10.88 ± 0.10	-73.00 ± 1.17
“	04.05.2017	3.31 ± 0.29	(-)	(-)

The $\delta\ ^{18}O$, $\delta\ ^{2}H$ and tritium isotope values of the springs range between -10.88 and -8.49 ‰, -74.28 and -63.41 ‰, 2.11 and 4.45 TU, respectively.

Figure 4 shows the ^{18}O-^{2}H graph for determine the origin of water [44-46]. The waters are generally located on the Ankara Meteoric Line (MWL) [44], so waters are meteoric origin. Otherwise, KM-K8 water has remained under some amount of Ankara Meteoric Water Line due to the enrichment with $\delta^{18}O$ and $\delta^{2}H$ because of evaporation an/or feeding from lower elevations compared to other waters.

When the tritium results of waters in the study area are appreciated using the assignation given in Table 3 [47], it can be determined that waters may have “mixture of half-modern and present recharge”. This is evidenced by the fact that the discharge of the waters have not increased much during the rainy season.

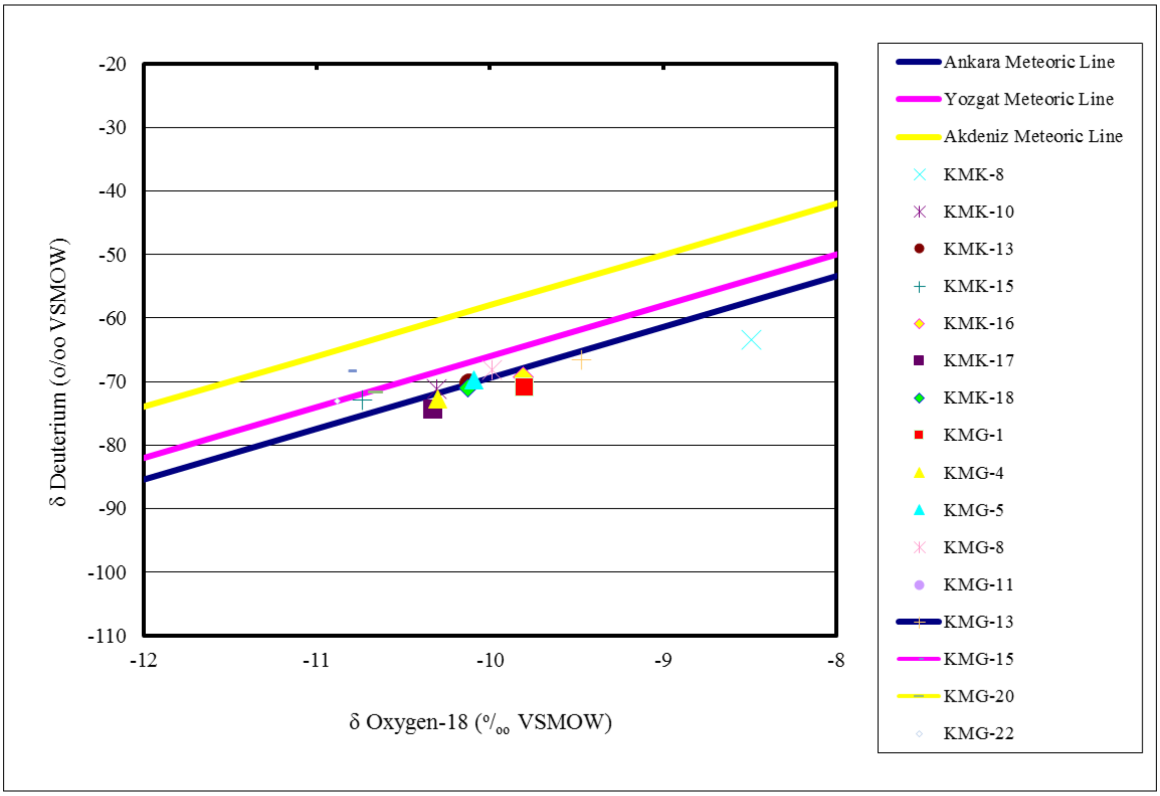

Figure 4 $\delta^{18}O$ – $\delta^{2}H$ graphs of groundwater large and/or discharging from Yemişliçay Formation in the study area **(**Ankara meteoric water line (MWL) from Sayın and Eyüpoğlu 2005 [44]**;** Yozgat MWL from Şimşek, 1993[45]; Mediterranean MWL from Payne and Dinçer 1965 [46]**)**

Table 3
Qualitative dating of groundwaters in continental regions (from Clark and Fritz 1997) [47]

Tritium Value (TU)	**Dating**
<0.8 TU	Submodern-recharged prior to 1952
0.8 -~4 TU	Mixture between submodern and recent recharge
5 -15 TU	Modern (<5 to10 yr)
15 – 30 TU	Some “bomb” ^{3}H present
>30 TU	Considerable component of recharge from 1960s or 1970s
>50 TU	Dominantly the 1960s recharge

6. CONCLUSION

This study aims to determine water pollution and hydrogeological proporties of Kaman (Kırşehir). While the conglomeratic and sandy levels are the grained aquifer, granites and syenites are fractured-cracked aquifers of the study area. The isotope analysis showed that the waters have generally meteoric origin and mixture of half-modern and present recharge.

In the study area, a lot of pollutants sources accompany each other and threaten public health. Many cancer cases are reported in the region. As revealed by the analysis, the study area has dual pollution sources natural pollution caused by water–rock interactions, and anthropogenic pollution originating from agricultural and mining activities, and these sources are effective processes resulting in water pollution. The concentrations of As, Sb, F, U, elements and NO_3, NH_4 ions in water samples exceed the Turkish and WHO drinking water standards. Pollutant levels of these elements were especially higher in groundwaters from discharging Kızılırmak and Meşeköy formations consisting of clastic rocks where were performed the agricultural activities. and magmatic rocks consisting of Fe, Sb, Au and F ores.

The As, Sb, F and U amount of waters vary between 0.3–398.4 ppb, 0.03–11.66 ppb, < 0.01–3.35 mg/L, 0.01–36.9 ppb, respectively. Especially it is thought that As contamination is a big problem for the region, because of tens of times exceed drinking water regulations. The sources of trace elements contamination in water discharging from magmatic and methamorphic rocks are the natural washings from ores/rocks. Furthermore, the mining process accelerates the dissolution of trace elements from the rocks. Also, there are two causes of As contamination waters which are discharging from clastic levels that have achieved agricultural activities. The first of these reasons is the water-rock interaction. The source rocks of the clastic levels are magmatic and metamorphic rocks in the upper elevations. The second is the anthropological pollution due to agricultural activities. The NH_4 values of waters vary between 0.09–1.99 mg/L, and the values are several times higher than value given in standarts in water discharging from the Kızılırmak and Meşeköy formations. Furthermore, generally, the NO_3 values of these are several times higher than the 50 mg/L value given in standards.

These contaminant resulting from mining and agricultural activities accumulate in the soil, percolate to the groundwater, and may increase over time. Furthermore it may cause the very important pollutation risk in terms of water and soil in the future. So, it is recommended that long-term environmental monitoring studies should be conducted in the area in terms of especially the As, Sb, F, U, NO_3 and NH_4 element/ion.

Acknowledgements

The authors would like to thank the Karabük University Scientific Research Projects Commission (BAP) for contributing to the financial portion of the project.

Funding

This project studies were supported by Karabük University Scientific Research Projects Commission. Project numbers were KBÜ-BAP-16/1-YL-091 and KBÜ-BAP-16/1-YL-092

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

This study is the master's thesis of Bahadır SUBAŞI and Feyza GİRİŞEN, and the idea of the studies belongs to supervisior that is Tülay EKEMEN KESKİN. Tülay EKEMEN KESKİN had a great contribution in providing support for the study, field studies, analyzing the waters, interpreting the findings and writing the thesis. Zeynel BAŞIBÜYÜK contributed during the fieldwork

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the article and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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