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QUALITY OF SOME SPRING WATERS IN ISTANBUL

İSTANBUL'DAKİ BAZI KAYNAK SULARININ KALİTESİ

Deniz KEY
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ABSTRACT: This article aims to determine the quality of spring waters in İstanbul and the convenience of these waters to human consumption. In order to evaluate spring waters in İstanbul in terms of the water quality, firstly labels of the bottled spring waters have been collected and studied, and general geological and environmental circumstances of İstanbul have been determined. In the year of 2011, there exist 53 bottled spring water producers in İstanbul. The indicator parameters on label informations of the bottled spring waters are compared with drinking and spring water limit values of WHO (2006), EPA (2009), EU (1998), TSE (2005) and Yönetmelik (2005), and it is seen that 22 of 53 spring waters exceed the limit values in terms of some parameters (Mn, Cl, SO_4, pH, Fe, Al and NH_4). It is observed that 40 of the springs emerge from sedimentary rocks, 9 from metamorphic rocks and 4 from volcanic rocks. SO_4 ion in spring waters in Çatalca emerging from metamorphic rocks, and Mn and Cl ions in spring waters in Eyüp and Şile emerging from sedimentary rocks generally are over the limit values. Moreover, pH value of some spring waters in Şile and Çatalca generally are under the limit values (<6,5). In addition, drainage areas of these springs are mostly covered by forests, while 16 springs are close to urban areas. It is the sedimentary rocks that spring waters in İstanbul where are mostly procured from and parameters which are over limit values are determined mostly in these waters. Therefore, the geology of the drainage areas of Hisar Water in Kemerburgaz and Kuvars Water in Maltepe whose aquifers are sedimentary rocks such as the Trakya and Aydos Formations have been investigated and chemical evaluation of the waters are conducted. In these investigations, quantities of heavy metals exceeding limit values and possibly having toxic effect have not been determined in the spring waters. However, possible increase of Fe, Mn, Al ions from weathering zones of the sandstone and graywackes of Trakya Formation in the drainage area of Hisar Water and possible increase of Fe ion from the limonite zones in fractures of the quartz arenites of Aydos Formation in the drainage area of Kuvars Water depending upon seasonal variations should be taken into consideration.

Key words: İstanbul, Spring Water, Label Informations, Heavy Metal

ÖZ : Bu çalışma, İstanbul'daki bazı kaynak sularının kalitesi ve bu suların tüketime uygunluğunun belirlenmesi kapsamında hazırlanmıştır. İstanbul'un kaynak sularının kalite yönünden değerlendirilebilmesi için öncelikle ambalajlı kaynak sularına ait etiketlere ulaşılmış ve İstanbul'un genel jeolojisi ve çevresel durumu belirlenmiştir. 2011 yılında, İstanbul'da 53 ambalajlı kaynak su üreticisi bulunmaktadır. Ambalajlı kaynak suların etiket bilgilerindeki gösterge parametreleri içme ve kaynak suyu limit değerleri [(WHO, 2006), (EPA, 2009), (EU, 1998), (TSE, 2005) ve (Yönetmelik, 2005)] ile karşılaştırıldığında 22'sinin bazı parametrelerce (Mn, Cl, SO_4, pH, Fe, Al ve NH_4) limit değerlerini aştığı görülmüştür. Kaynak sularının boşalım yaptığı litolojiler dikkate alındığında 40'ının sedimenter, 9'unun metamorfik ve 4'ünün ise volkanik kayaçlar ile etkileşimde olduğu belirlenmiştir. Genel olarak, Çatalca'nın metamorfik kayaçlarından gelen kaynak sularında SO_4, Eyüp ve Şile'nin sedimenter kayaçlarından gelen kaynak suların ise Mn ve Cl iyonlarının limit değerlerince yüksek olduğu görülmüştür. Ayrıca, Şile ve Çatalca'nın bazı kaynak sularında pH değeri de limit değerlerin altında (<6,5) kalmaktadır. Firmaların üretim yaptığı beslenim alanlarında çoğunlukla ormanların olduğu ancak, 16 su tesisinin yerleşim alanlarına yakın konumlarda bulunduğu belirlenmiştir.

İstanbul'da kaynak suyun en çok sağlandığı ve yine en çok bu sularda limit değerleri aşan parametrelerin tespit edildiği birim sedimenter kayaçlardır. Bu nedenle, akiferleri Trakya ve Aydos Formasyonları gibi sedimenter kayaçlar olan Kemerburgaz'daki Hisar Su ile Maltepe'deki Kuvars Su beslenim alanlarının jeolojisi incelenmiş ve suların kimyasal değerlendirilmesi yapılmıştır. Yapılan incelemelerde kaynak sularında limit değerleri aşan ve toksik etkisi olabilecek ağır metal miktarları belirlenmemiştir. Ancak, Hisar Su beslenim alanında, Trakya Formasyonuna ait kumtaşı ve grovaklardaki ayrışma zonlarından Fe, Mn, Al iyonlarının; Kuvars Su'yun beslenim alanındaki Aydos Formasyonuna ait kuvarsarenitlerin çatlaklarındaki limonit zonlarından ise Fe iyonunun mevsimsel değişimlere bağlı olarak sularda artabileceği dikkate alınmalıdır.

Anahtar Kelimeler: İstanbul, Kaynak Suyu, Etiket Bilgileri, Ağır Metal

INTRODUCTION

This article includes only a part of the study that is prepared as the graduate thesis at the Geological Engineering Division of Sciences Institute of İstanbul University in the years 2009-2011. With the survey, label informations of the spring waters in İstanbul being sold for to the public consumption have been evaluated in order to reveal the quality of spring waters of İstanbul. It is determined that there exist 53 companies in İstanbul that are producing bottled spring water, 29 of which are located in the Anatolian side, and 24 of which are in the European side (Table 1). Spring water companies release most of their licensed and bottled spring waters with demijohns (19 lt polycarbonate bottle) to public's consumption by taking care of convenient pyhsical and chemical conditions that will not threaten the public health. In Turkey, so far, although there have been various surveys about water chemistry and geochemistry made and their results have been published, limited number of research has been made about the water quality of the spring water's consumption which is produced as demijohn type in İstanbul. The studies regarding to İstanbul and its vicinty are investigated, it is seen that first studies have been made for hydrogeological (Eroskay, 1978; Yüzer et al., 1992; Özler, 2008, Öztaş, 2008) and environmental (Atalık, 2008) purposes.

Table 1. The companies which produce bottled spring water in İstanbul
Çizelge 1. İstanbul'daki şişelenmiş kaynak suyu üretimi yapan firmalar

	COUNTY	*SPRING WATER COMPANIES*
EUROPAN SIDE	**EYÜP**	Başpınar, Kumsu, Kemer, Fındıksu, Hisar, Hamidiye Şifa, Güvenpınar, Hamidiye, Hamidiye Burgaz, Sunmercan and Çobanpınar
	ÇATALCA	Akçapınar, Mispak, Ulupınar, Minella, Altınpınar, Gümüşpınar, İmren, Ayazma and Yalısu
	SARIYER	Kestane
	SULTANÇİFTLİĞİ	Güzelpınar
	ARNAVUTKÖY	Özpınar
	SİLİVRİ	Buzada
ANATOLIAN SIDE	**ŞİLE**	Taşpınar, Türkkızılayı, Akpınar, Nisa, Saray, Kervansaray, Emirdağ, Kırkpınar, Zambak, Özlempınar, Kovanpınar, İpekpınar, Beyza Taşdelen and Aquanet
	BEYKOZ	Akasya, Karakulak, Sırmakeş, Kayla, Koçbey Aqua, Haznedar and Çubuklu
	MALTEPE	Kuvars, Florist, Özkayışdağ, Çamlıbeldeki Gözeler
	KARTAL	Aydos Çamoluk and Taşeren
	PENDİK	Beys
	ÇEKMEKOY	Taşdelen Vakıf

Results of the water analysis of some tap and well water throughout İstanbul have been evaluated by Örgun and Uğur (1996) and it is determined that water throughout the city is rich of Ca, Mg, Na+K cations, and limit values (TS 266) have been exceeded for quantities of pH, NH_4, NO_2 and organic materials in waters.

Label informations of 103 bottled water throughout Turkey which is intended for consumption have been evaluated by Pehlivan (2007), it was found that Fe, Zn, As, and Al ions in some spring water and mineral water over the limit values of World Health Organisation (WHO, 2006), European Union (EU, 1998) and Turkish Standarts (TSE 266, 2005). The researcher, also determined that Fe and As ions on label informations of Hisar and Şadırvan spring waters exceed the recommended limit values (Pehlivan, 2007).

In order to determine the convenience for consumption of spring and drinking waters which are sold in İstanbul and near vicinity, major ions and certain anionic components of bottled waters have been analysed by Güler et al. (2008). pH values of the three of analysed water samples have been determined to be under the limit value of CD (98-83-EC), while one of the sample's As concentration has been exceeded by three times the limit values of CD (98-83-EC).

Therefore, firstly, the bottled spring waters of İstanbul have been evaluated according to the label informations on packages and interaction of the waters between geological units and environmental conditions have been determined. Secondly, in the graduate thesis project (Key, 2011), hydrogeochemical investigations were done at the two springs where were extracted from Trakya and Aydos Formations which are the two important aquifers of İstanbul. In this study, detailed geological investigations was carried out in the vicinities of the water wells which belong to Hisar Water company from the European side and Kuvars Water company from the Anatolian side. Moreover, heavy metals (Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Zn, Cu, Se, Sb, B, Mo and U) of the spring waters have been analysed in order to determine the interaction of geological units to the water quality.

MATERIAL AND METHOD

Label informations which belong to spring waters have been procured by purchasing the bottled water from markets. In order to reveal the influence of geological units to water quality, 1/10000 scale of geological maps have been prepared and, rock and soil samples have been collected from vicinities of the water drilling wells of Hisar Water and Kuvars Water. Moreover, water samples have also been taken from the drill holes in September 2009 and December 2009 periods. The spring waters have been filled into the 0,5lt plastic bottles for analysing their heavy metal concentrations. Then, pH values of the bottled spring waters have been processed with nitric acid (HNO_3) in order to attain their pH values of 2 and the waters have been protected. Quantities of trace elements of the rock and soil samples (Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Zn, Cu, Se, Sb, B and U) and heavy metals in the spring waters (Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Zn, Cu, Se, Sb, B, Mo and U) have been analysed by ALS Chemex (İzmir). Additionally, mineralogical and petrographical investigations of the host rock samples have been determined with polarized microscope, and the soil samples have been conducted with XRD diffraction in İ.Ü. Advance Analysis Laboratory.

BOTTLED SPRING WATERS OF ISTANBUL

Spring water is described as the water that discharges by itself from one or more points in nature and its chemical composition could change by precipitation, geological units and environmental

circumstances. However, in Our Country, springs could not supply public's drinking water requirement enough in the big cities. Hereby, usual description of spring water has been redefined in the Yönetmelik (2005). According to the Regulation Concerning Water Intended for Human Consumption (Yönetmelik, 2005), spring water is defined as the water that can be emerged with technical methods without altering its quality. According to the legal definition, most of the water companies in İstanbul procure their water from water drilling wells. The companies also release their waters to public as packaged, in order not to derogate the water quality without any disinfection process except for some ozonization and filtration. Although the number of spring water products in İstanbul for the year 2011 is 53, the real number of operating companies is 50, because Kuvars, Sırmakeş and Hisar water companies operate their second brand by names of "Florist", "Kayla" and "Hamidiye Şifa", respectively (Table 1).

1. LABEL INFORMATION OF THE SPRING WATERS

In order to evaluate the qualities of bottled spring waters in İstanbul, certain physical and chemical parameters from the indicator parameters on labels such pH, chloride (Cl^-), sodium (Na^+), sulphate (SO_4^{2-}), iron (Fe^{2+}), aluminium (Al^{3+}), manganese (Mn^{2+}), ammonium (NH_4^+) and conductivity (µS/cm) have been considered. Each data obtained from indicator parameters have been compared with the limit values of drinking water World Health Organization (WHO, 2006), U.S. Environmental Protection Agency (EPA, 2009) and European Council (CD 98/83/EC) and of spring water Turkish Standards (TSE, 2005) and The Regulation Concerning Water Intended for Human Consumption (Yönetmelik, 2005) (Table 2).

Table 2. The spring water limit values according to WHO (2006), EPA (2009), CD (98/83/EC), TSE (2005) and Yönetmelik (2005) (ppm)

Çizelge 2. WHO (2006), EPA (2009), CD (98/83/EC), TSE (2005) ve Yönetmelik (2005)'e göre kaynak suyu limit değerleri (ppm)

	WHO 2006	EPA 2009	CD 98/83/ EC	TSE (2005)	Yönetmelik (2005)
	Drinking Water	Drinking Water	Drinking Water	Spring Water	Spring Water
pH	6,5-8,5	6,5-8,5	6,5-9,0	6,5-9,5	6,5-9,5
Cl^-	250	250	250	30	250
Na^+	200	X	200	100	200
SO_4^{2-}	500	250	250	25	250
NH_4^+	X	X	0,5	0,05	0,5
Al^{3+}	0,1	0,2	0,2	0,2	0,2
Sb^{3+}	0,005	0,006	0,005	0,005	0,005
As^{3+}	0,01	0,01	0,01	0,01	0,01
Cu^{2+}	2	1,3	2	0,1	2
Ba^{2+}	0,7	2	X	X	X
B^{3+}	0,3	X	1	1	1
Hg^{2+}	0,001	0,002	0,001	0,001	0,001
Zn^{2+}	0,1	5	X	X	X
Fe^{2+}	0,3	0,3	0,2	0,05	0,2
Ag^+	0,005	0,1	X	X	X
Cd^{2+}	0,003	0,005	0,005	0,005	0,005
Cr^{3+}	0,05	0,1	0,05	0,05	0,05
Co^{2+}	X	X	X	X	X
Pb^{2+}	0,01	0,015	0,01	0,01	0,01
Mn^{2+}	0,5	0,05	0,05	0,02	0,05
Mo^{6+}	0,07	X	X	X	X
Ni^{2+}	0,02	X	0,02	0,02	0,02
Se^{2-}	0,01	0,05	0,01	0,01	0,01
U^{6+}	0,015	0,03	X	X	X
Con*	X	2500	2500	650	2500

Explanation: * Conductivity (µS/cm); X: No data

2. GEOLOGICAL EVALUATION

In order to determine the influence of the host geological units on the chemistry of spring waters, locations of the spring waters have been shown on the 1/100000 scale of simplified geological map. To compile the simplified geological map, maps of Oktay and Eren (1994) and MTA (2002) have been used. According to this simplified map, surface area of İstanbul consists of 80% sedimentary rocks, 10% metamorphic rocks, 7% volcanic rocks and 3% magmatic rocks (Figure 1).

In the European side, 9 spring water companies are located in Çatalca where metamorphic rocks of the Strandja Massif outcrop. These metamorphic units are either directly the aquifer for the spring waters, or outcrop at upstream sides of the spring water drainage areas. The spring water drainage

areas of Özlempınar, Kovanpınar, İpekpınar and Aquanet companies are located in the northern part of the Anatolian side where volcanic rocks outcrop (Figure 1). The volcanic rocks consist of pyroclastic breccia, flow breccia, hyloclastite, pyroclastic flow deposits, felsic tuff and volcanic originated sandstone (Yavuz and Yılmaz, 2010).

At the drainage areas of other 40 spring waters in İstanbul, sedimentary rocks outcrop (Figure 1). In the Europan side, aquifers of 10 springs in the Alibeyköy and Kâğıthane drainage areas and of the springs of Güzelpınar and Özlempınar are the Trakya Formation of Lower Carboniferous in age, which consists of graywacke, sandstone, conglomerate and limestone (Kaya, 1971). The aquifers of all springs which are located in southern part of the Anatolian side and of the springs of Kestane, Çubuklu, Vakıf and Beyza Taşdelen, are the Aydos Formation of Middle Ordovician in age which consists of quartz arenites (Önalan, 1981).

In İstanbul, there are various quarries where some materials such as aggregate, coal, clay, quartzite are mined. At the Europan side, one of the quarries is located close to Güzelpınar spring water site, some other quarries are also located at the upstream sides of Sunmercan and Hamidiye Burgaz springs (Figure 1). It is known that mineral dust from mining activities, affect the human health negatively. Therefore, water quality in any spring water filling factory which is close to any quarry or mine area will also be affected negatively by the mineral dusts carried by wind.

3. ENVIRONMENTAL EVALUATION

The locations of spring water production establishments and forest, rural, residential and industrial areas have been determined by updated satellite pictures of the official web site of İstanbul Metropolitan Municipality (İBB., 2011). These data are shown on a 1/100000 scale map (Figure 2) is used to evaluate the environmental conditions of İstanbul. This evaluation, showed that nearly 20% of İstanbul consists of residential and industrial areas, 25% is rural and agricultural areas, 5% is water reservoir areas (dams and lakes) and the rest 50% of forest and woody areas. Most of the springs are in regions covered by forest. But, some residential areas are also situated at upstream sides of some spring water drainage areas (Figure 2). It is determined that 16 production establishments of spring waters such as Başpınar, Kemer, Fındıksu, Kumsu, Hamidiye and Hamidiye Burgaz in the Kâğıthane creek drainage area in Eyüp and Ulupınar, Mispak, Gümüşpınar, Buzada, Kestane, Taşeren, Aydos Çamoluk, Beys, Türkkızılayı and Taşpınar are located in urban areas or in the downstream sides of them (Figure 2).

4. WATER QUALITY OF THE SPRING WATERS

The evaluation of the bottled spring waters produced in İstanbul in terms of water quality has been performed by comparing the indicator parameters on the packages with the drinking and spring water limit values and by regarding geological and environmental conditions influencing water quality in a positive or negative manner.

According to the label information, 31 of the spring waters produced in İstanbul are within the limit values (WHO 2006, EPA 2009, CD 98/83/EC, TSE 2005 and Yönetmelik, 2005) by Key (2011). According the lithologies, where spring waters emerge from, 25 springs emerge from sedimentary rocks, 3 springs emerge from metamorphic rocks (The Strandja Massif) and 3 springs emerge from volcanic rocks (İstanbul volcanites). All these regions are mostly covered with forest and are rural areas far away from the urban areas.

On the other hand, some parameters of 22 bottled spring waters exceed the limit values of drinking and spring water. pH values of 7 spring waters are under the limit values according to WHO (2006), EPA (2009), CD 98/83/EC, TSE (2005) and Yönetmelik (2005), while Mn, Cl, SO_4, Fe and NH_4 are in respectively 10, 7, 3, 1 and 1 of the waters over the spring water limit values according to TSE (2005), and Al is in 1 of the waters over the drinking water limit values according to WHO (2006) (Table 2 and Table 3).

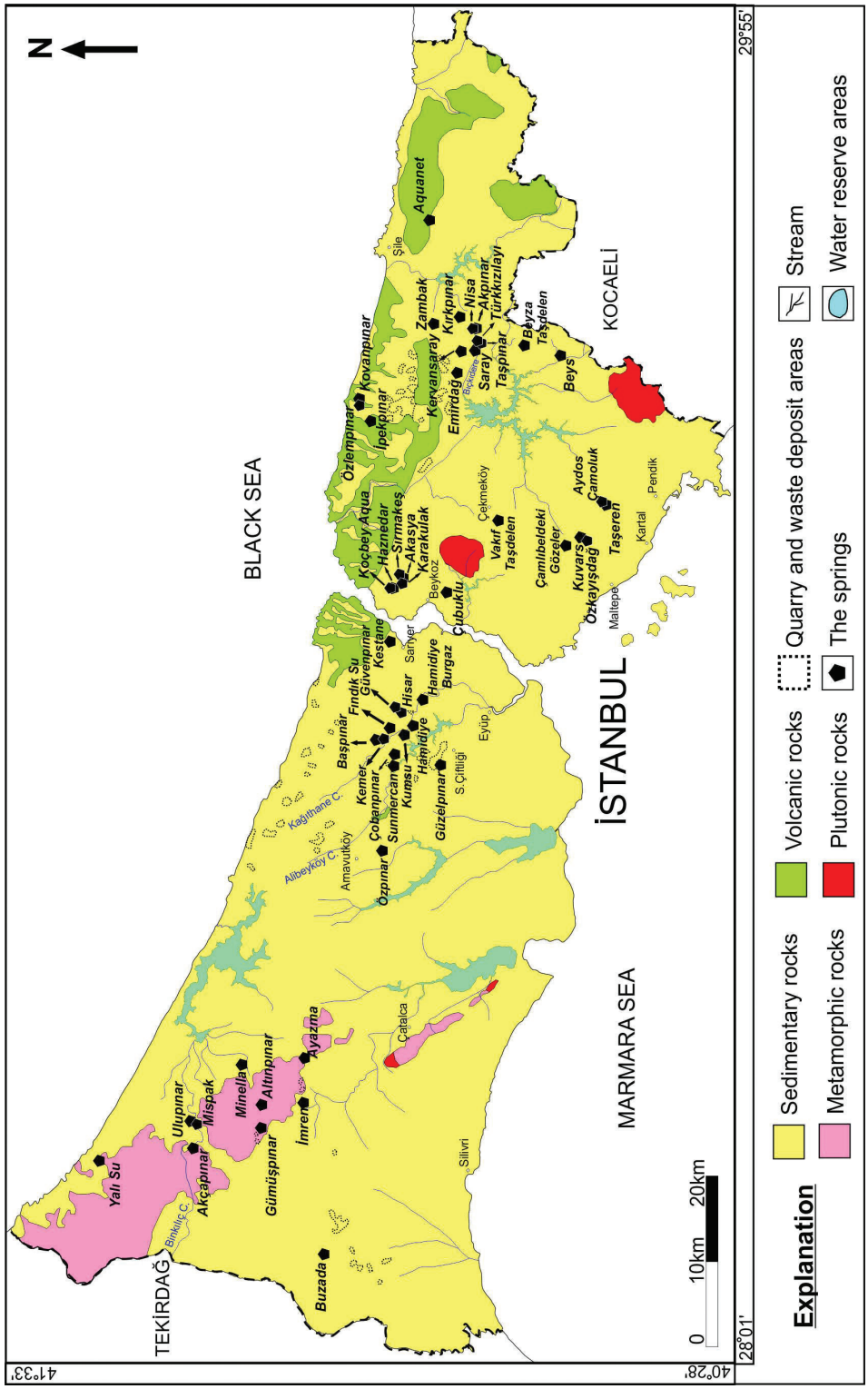

Figure 1. The map which shows distribution of geological units which are outcropped in İstanbul and locations of the packaged spring water production facilities

Şekil 1. İstanbul'da mostra veren jeolojik birimlerin dağılımı ile ambalajlı kaynak su imla tesislerin lokasyonlarını gösterir harita

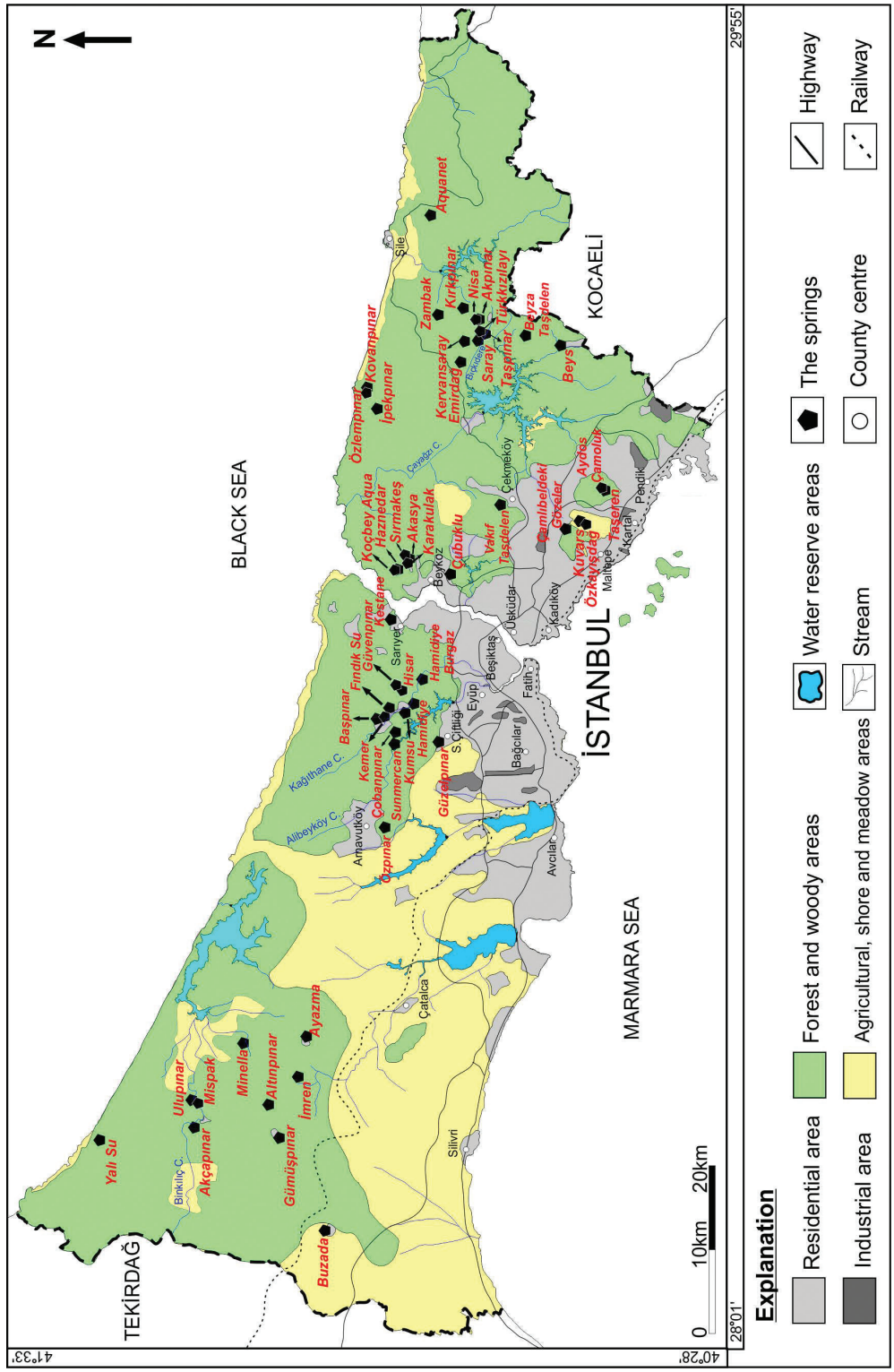

Figure 2. The map which shows distribution of forest, agriculture and urban areas in İstanbul and locations of the packaged spring water production facilities

Şekil 2. İstanbul'un orman, tarım ve yerleşim alanlarının dağılımı ile ambalajlı kaynak su imla tesislerin lokasyonlarını gösterir harita

In some spring waters (Ulupınar, Ayazma and Yalısu) that emerge from metamorphic rocks in Çatalca, SO_4 and Mn ions are over the limit values of TSE (2005). In addition, some parameters in spring waters that emerge from sedimentary rocks, limit values of the WHO (2006) and TSE (2005) are exceeded. For example, in some spring waters (Başpınar, Hamidiye Şifa and Sunmercan) where the Trakya Formation is the aquifer, SO_4, Mn and Al, in some spring waters (Türkkızılayı, Akpınar, Nisa and Emirdağ) of Şile, Mn and also in one spring water (Taşeren) where the Aydos Formation is the aquifer, Fe and Mn quantities are out of the limit values (Table 3). It is considered that, some trace elements (Al, Fe, Mn, As, Hg, Co, Cd, Cr, Pb, Ni, Ti, Ba, Zn, Cu, U etc.) are in the geological units (volcanic, metamorphic, plutonic and sedimentary rocks) can influence water as heavy metals and change the water quality adversely (Pehlivan and Yılmaz, 2005).

Off-limit values of pH and Cl in some spring waters (Mispak, Minella, Gümüşpınar, Kumsu, Hamidiye Şifa, Sunmercan, Kovanpınar, Taşpınar, Türkkızılayı, Emirdağ, Kervansaray and Beyza Taşdelen) in Çatalca, Eyüp and Şile counties could be explained by water drilling wells are fed by shallow groundwaters or surface waters which are close to rain water composition. Another reason why both of parameters are kept out of the recommended limit values, could be quality of shallow groundwaters influenced adversely by antropogenic liquid waste arising from existance of inhabiting areas in some drainage areas. Likewise, being high of NH_4 amount in Buzada could be related with existance of inhabiting areas (Table 3).

Table 3. The label informations of bottled spring waters which are produced in İstanbul
Çizelge 3. İstanbul'da üretilen şişelenmiş kaynak suların etiket bilgileri

Commercial Name	**Mispak**	**Ulupınar**	**Minella**	**Gümüşpınar**	**Ayazma**	**Yalı Su**	**Buzada**	**Başpınar**
County	Çatalca	Çatalca	Çatalca	Çatalca	Çatalca	Çatalca	Silivri	Eyüp
Villiage	Karamandere	Karamandere	Çiftlikköy	Gümüşpınar	Akalan	Yalıköy	Beyciler	Göktürk
Permit Date	21.01.2008	01.04.2008	08.04.2008	07.06.2010	17.02.2005	02.04.2007	27.10.2010	30.05.2006
Permit Number	136	167	170	KS.34.42	25730	44	KS.34.53	12
pH	**6,2**	6,51	**6,25**	**5,56**	7,72	6,5	8	6,6
Cl- (mg/l)	ND	25,45	19,26	14,53	26	23,78	**44,98**	22,8
Na^+ (mg/l)	10,82	15,05	11,83	9,3	94,98	14,2	56,6	19,7
SO_4^{2-} (mg/l)	2,01	16,59	1,8	6,2	**37,5**	**40,3**	18,52	6,2
NH_4^+ (mg/l)	ND	Absent	Absent	0	Absent	0	**0,5**	Absent
Fe^{2+} (µg/l)	3,73	27,38	< 2	<2	4,3	2,08	47,3	Absent
Al^{3+} (µg/l)	1,53	48,38	< 3	27,5	3,9	8,73	18,2	Absent
Mn^{2+} (µg/l)	5,68	**39,57**	2,4	<2	< 2	4,3	**39,1**	**31**
Con. (µS/cm)	102	183,3	69	90,4	333	127,4	489	204

Table 3 (continues)

Commercial Name	**Kumsu**	**Hamidiye Şifa**	**Sunmercan**	**Özpınar**	**Sırmakes**	**Kovanpınar**	**Taşpınar**
County	Eyüp	Eyüp	Eyüp	Arnavutköy	Beykoz	Şile	Şile
Villiage	Kemerburgaz	Kemerburgaz	Pirinççi	Boğazköy	Dereseki	Kurnakoy	Bıçkıdere
Permit Date	22.07.2010	20.04.2010	05.05.2008	21.06.2006	31.03.2008	17.06.2010	13.10.2006
Permit Number	KS.34.51	KS.34.35	178	16	166	KS.34.44	35
pH	7,1	6,6	6,85	7,9	7,28	**6,35**	**6,1**
Cl- (mg/l)	**39,25**	**42,6**	**30,1**	**34,87**	13,1	29	15,04
Na^+ (mg/l)	24,5	6,72	25,48	29,65	7,69	15,4	9,29
SO_4^{2-} (mg/l)	17,3	**34,13**	15,81	17,41	3,96	3,86	3,82
NH_4^+ (mg/l)	0	<0,05	Absent	-	0	<0,05	0,02
Fe^{2+} (µg/l)	32,6	<11	29,7	17,6	<0,3	<0,3	8,8
Al^{3+} (µg/l)	9,1	3,94	**134,7**	9,3	<0,3	3	Absent
Mn^{2+} (µg/l)	1,5	<0,6	**33,8**	-	**25,12**	19,32	Convenient
Con. (µS/cm)	287	63,8	306	264	80,2	130,9	119,5

Table 3 (continues)

Commercial Name	**Türkkızılayı**	**Akpınar**	**Nisa**	**Emirdağ**	**Kervansaray**	**Beyza Tasdelen**	**Taseren**
County	Şile	Şile	Şile	Şile	Şile	Şile	Kartal
Villiage	Bıçkıdere	Bıçkıdere	Bıçkıdere	Kömürlük	Kervansaray	Bıçkıdere	Yakacık
Permit Date	28.05.2010	08.10.2009	14.01.2008	02.07.2010	11.01.2008	07.05.2010	18.12.2007
Permit Number	KS.34.39	KS.34.05	132	KS.34.49	130	KS.34.37	106
pH	**6,38**	6,9	6,5	7	7,6	**6**	7,19
Cl^- (mg/l)	10,1	11	14,34	**31,03**	**80,9**	21,6	10,5
Na^+ (mg/l)	7,4	7,34	8,59	21,04	55,4	13,7	10,62
SO_4^{2-} (mg/l)	3,57	3,01	3,63	3,25	4,98	5,4	14,4
NH_4^+ (mg/l)	0	0	ND	0	0	0	Absent
Fe^{2+} (µg/l)	<0,3	7	8,33	8,85	5,6	0	**62,86**
Al^{3+} (µg/l)	<0,3	5	7,86	10,86	0	31,5	<0,3
Mn^{2+} (µg/l)	**38,1**	**23,8**	**27,94**	**38,43**	0,02	3,42	**38,33**
Con. (µS/cm)	89,3	105,3	111,3	205	360	136	152,6

Explanation

Bold numbers show values over limit; ND. Not defined; - : No data

DETAILED GEOLOGICAL INVESTIGATION OF THE HISAR AND KUVARS SPRING WATERS

It is determined that various parameters of spring waters in İstanbul which discharge from sedimentary rocks exceed the limit values. Therefore, a detailed geological investigation has been performed in the drainage areas of two different springs, which emerge from sedimentary rock aquifers. The respective water companies are Hisar Water in Kemerburgaz at the European side and Kuvars Water in Maltepe at the Anatolian side. When locations of producing wells are considered, Hisar Water and Kuvars Water procure their water from Kurudere and Çamurlukdere drainage areas, respectively (Figure 3).

1. HISAR WATER

1.1. General Geological Investigation

The oldest unit of the Kurudere drainage area is the Trakya Formation, deposited in flysch facies of deep marine conditions and Lower Carboniferous in age (Kaya, 1971). Trakya Formation consists of sandsones including yellowish, grey coloured graywacke-shale levels, and some polygenic conglomerates and limestones. In such places as Develi Hill, the Belgrat Formation that occures discordantly over the Trakya Formation, has Pliocene in age and comprise red coloured sand and gravel. Moreover, the youngest unit of the observing area is Quaternary in age alluviums including unconsolidated and poor sorted silt, sand and gravel clastics (Figure 3).

1.2. Mineralogical ve Petrographic Investigation

8 rock samples (H1wr, H2wr, H3wr, H4wr, H5wr, H7wr, H9wr and H10wr) and 2 soil samples (H6s ve H8s) have been collected from the Kurudere drainage area (Figure 3). In respect of the thin sections of the sandstones, the rocks consist of 65% quartz, 25% plagioclase, muscovite and chloride, and 10% opaque minerals and clay-silt grain sized clastics. According to the XRD diffractograms, the soils include 95% quartz, 3% plagioclase (anorthite type) and 2% minerals such as chloride, kaolinite and illite.

1.3. Lithogeochemical Investigation

According to average quantities of the trace elements of rock and soil samples, the amounts of Al, Ba, Cd, Cu, Fe, Mn, Mo, Ni and Zn exist in the rocks are more than of the soil, while Sb, As, Cr, Co, Pb, Hg, Se, Ag and U quantities in the soil are more than of the rocks (Table 4).

Table 4. The results of trace element analysis of rock and soil samples which are in the Kurudere drainage area (ppm) (wr: rock sample, s: soil sample)
Çizelge 4. Kurudere drenaj alanındaki kayaç ve toprak örneklerinin iz element analiz sonuçları (ppm) (wr: kayaç örneği, s: toprak örneği)

	H1 wr	H2 wr	H3 wr	H5 wr	H9 wr	H10 wr	H6 s	H8 s
Al	73700	90200	60400	59600	96200	61700	54500	59100
Sb	1,34	1,03	0,65	0,44	0,82	0,47	0,97	0,97
As	8,9	15,9	7,2	3,8	10,7	2,2	10,6	13,1
Cu	23,7	74,4	24,8	15,7	59,9	16,5	20	15,2
Ba	300	510	380	220	570	210	260	340
Hg	<0,01	0,01	<0,1	<0,1	<0,1	<0,01	0,03	0,03
Zn	88	102	74	53	115	60	54	54
Fe	44100	60400	44900	36900	68400	34800	34200	33100
Ag	0,08	0,08	0,03	0,05	0,07	0,07	0,09	0,09
Cd	0,17	0,75	0,06	0,04	0,04	0,05	0,05	0,05
Cr	87	119	80	67	135	72	149	135
Co	13,6	16,2	28,1	14	19,9	8,1	15,4	19,5
Pb	21,4	18	10,7	5,8	15,2	9,6	23,5	23,8
Mn	803	857	1410	948	1380	438	548	1230
Mo	4,28	1,61	1,06	0,56	0,5	0,45	1,26	1,31
Ni	42	69,3	48,5	32,5	73,1	28,5	37,1	43,6
Se	1	2	1	2	3	2	2	2
U	1,3	1,9	1	0,9	1,7	1	2,1	2,4

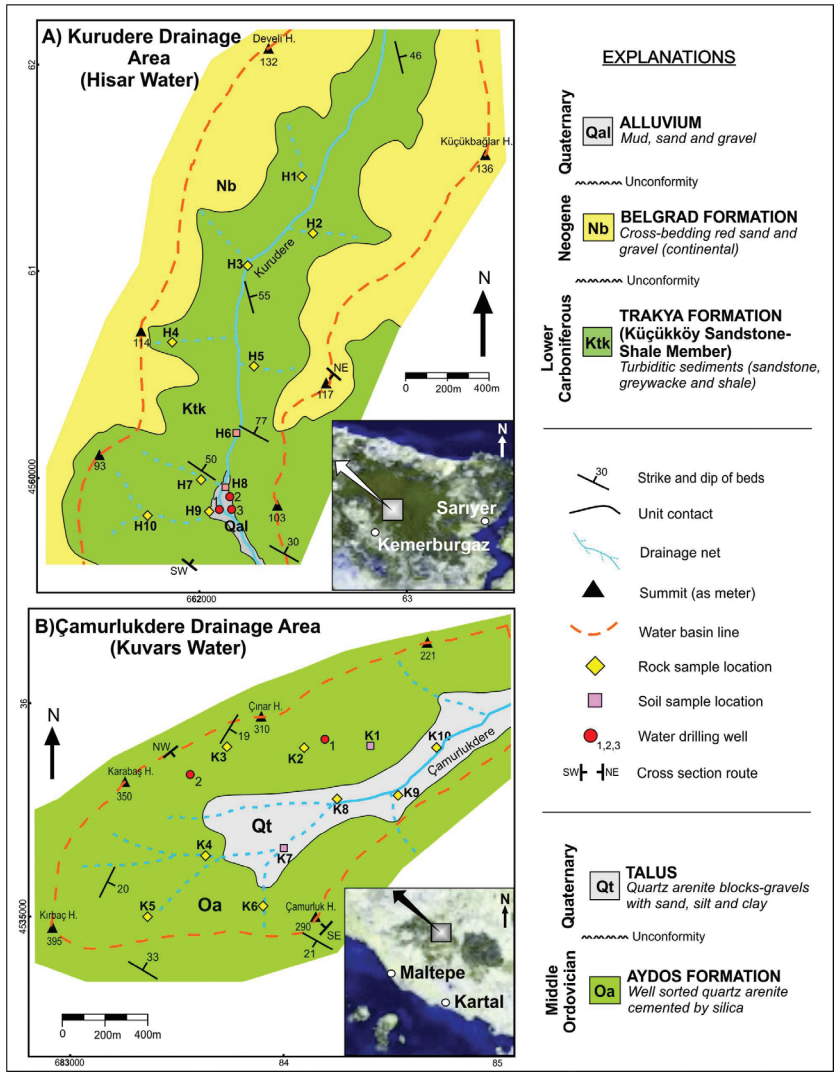

Figure 3. The 1/10000 scale of the geological maps of Hisar Water (A) and Kuvars Water (B) drainage areas
Şekil 3. Hisar Su (A) ve Kuvars Su (B) drenaj alanlarının 1/10000 ölçekli jeoloji haritaları

1.4. Hydrogeochemical Investigation

Precipitations feed the groundwater in the Küçükköy sandstone-shale member by infiltrating and leaking through the dip direction of the beds. The sandstone and graywacke levels of the unit are the aquifer as they have secondary porosity and water is obtained by drill holes in these units (Figure 4). Heavy metal quantites in the water have been determined by water samples taken from the 3th water drill hole of the Hisar Water company in September 2009 and December 2009 (Table 5). From September through December, quantities of As, Ba, B, Cu, Pb, Mn, Mo, U, Zn and Ag ions increase, where as the quantities of Al, Co, Fe and Ni ions decrease. Analysis of heavy metal quantities in water samples of both periods have been compared with limit values. It is determined that Fe quantity in September period was over the limit value according to TSE (2005).

Table 5. The results of heavy metal analysis of spring water which sampled from the 3th well of Hisar Water (ppb)

Çizelge 5. Hisar Su'ya ait 3 nolu kuyudan alınan kaynak suyunun ağır metal analiz sonuçları (ppb)

	September 2009	December 2009
Al^{3+}	54,1	11,3
Sb^{3+}	<0,1	<0,1
As^{3+}	0,47	0,79
Ba^{2+}	13,8	28,1
B^{3+}	11	43
Cd^{2+}	<0,05	<0,05
Cr^{3+}	2,54	<3
Co^{2+}	0,26	0,24
Cu^{2+}	<0,90	2,39
Fe^{2+}	61	<30
Pb^{2+}	0,273	0,383
Mn^{2+}	2,33	6,96
Mo^{6+}	<0,05	0,138
Hg^{2+}	<0,05	<0,05
Ni^{2+}	5,5	4,53
Se^{2-}	<1	<1
Ag^{+}	<0,010	0,014
U^{6+}	0,018	0,099
Zn^{2+}	<5	14,3

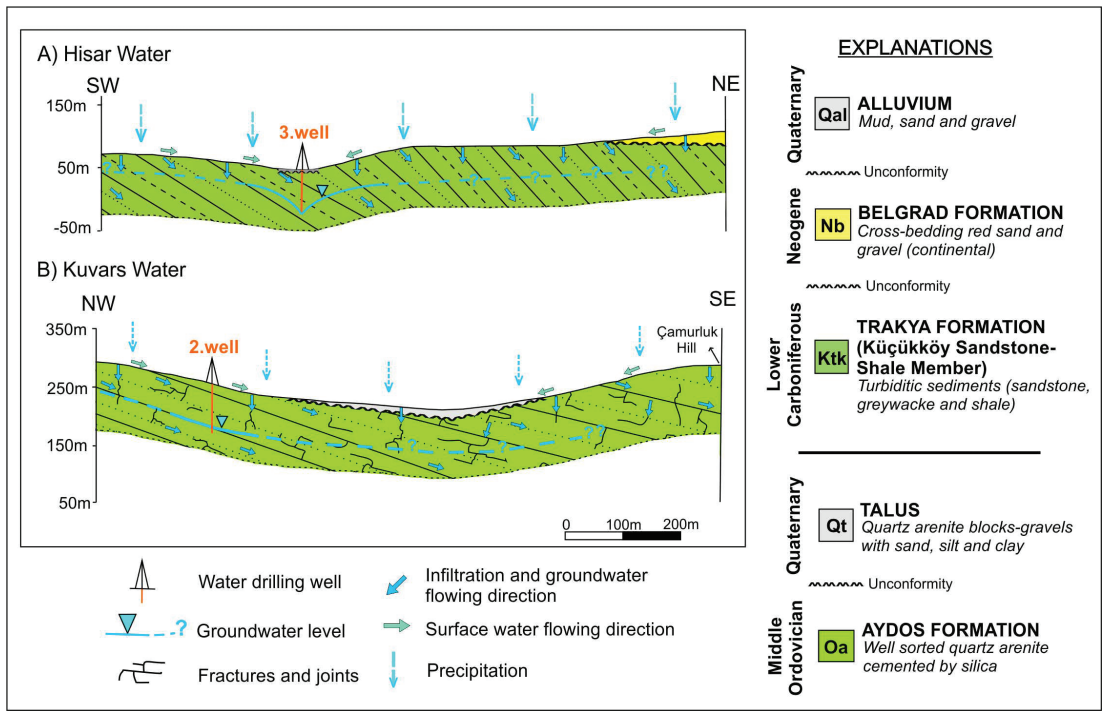

Figure 4. The 1/10000 scale of the geological cross sections of Hisar Water (A) and Kuvars Water (B) drainage areas

Şekil 4. Hisar Su (A) ve Kuvars Su (B) drenaj alanlarının1/10000 ölçekli jeolojik enine kesitleri

2. KUVARS WATER

2.1. General Geological Investigation

The basic rock of the Çamurlukdere drainage area is the Aydos Formation (Figure 3), formed in coastal and high energical shallow marine conditions of the Middle Ordovician in age and comprise white and beige coloured quartz arenites (Önalan, 1981). According to field observations, fracture planes in the rocks get brown, yellow and redish colour by influence of Fe ion in the water. The youngest unit of the study area is Quaternary in age talus whose thickness can reach 15 m on the stream bed (Figure 4). The talus consist of the quartz arenite blocks of the Aydos Formation. Blocks are also generally in 10-15 cm diameter and are cemented by redish sand and clay sized clastics.

2.2. Mineralogical ve Petrographic Investigation

8 rock samples (K2wr, K3wr, K4wr, K5wr, K6wr, K8wr, K9wr and K10wr) and 2 soil samples (K1s and K7s) have been collected from the Çamurlukdere drainage area (Figure 3). In respect of the thin sections of the quartz arenites, the rocks consist of 95% well sorted and spherical quartz grains and the grains are cemented by limonite and quartz clasts. Moreover, 1-5% opaque minerals, clastics and feldspar have also been determined in the mineral composition of the rock. According to the XRD diffractograms of the soil samples, soils commonly include 95% quartz and 5% plagioclase and illite.

2.3. Lithogeochemical Investigation

All trace elements (Al, Ba, Cd, Cu, Fe, Mn, Mo, Ni, Zn, Sb, As, Cr, Co, Pb, Hg, Se, Ag and U) are richer in the soil samples than the rock samples (Table 6). It is expected that trace elements in the quartz arenites should be low due to their formation in a high energical shallow and clear coastal environment. However, trace elements increasing in the soil could result from quartz clasts being transported away by erosion.

2.4. Hydrogeochemical Investigation

The Aydos Formation has hard and brittle features because of high amount of quartz minerals 95%. These properties have two important concequences that affect the feeding conditions of groundwater. Firstly, quartz arenites form topographic heights (Kıbaç Hill etc.) of the region by having hardness and resistance against erosion and these heights occure the water sources of the region. Secondly, the unit has fractures and joints due to it is brittle structure, and drill holes of Kuvars Water are fed by these discontinuity levels. Moreover, heavy metal quantities of the water are affected directly by precipitation and geochemical - mineralogical specialities of quartz arenites (Figure 4). Heavy metal quantites have been determined by water samples taken from the 2nd drill hole of Kuvars Water company in September 2009 and December 2009 (Table 7). From September through December, quantities of Al, As, Ba, B, Co, Cu, Fe, Pb, Mn, Ni and Zn ions increase, where quantity of Ag ion decreases. At the same time, Fe quantity in the December period was over the limit value according to TSE (2005).

Table 6. The results of trace element analysis of rock and soil samples which are in the Çamurlukdere drainage area (ppm) (wr: rock sample, s: soil sample)

Çizelge 6. Çamurlukdere drenaj alanındaki kayaç ve toprak örneklerinin iz element analiz sonuçları (ppm) (wr: kayaç örneği, s: toprak örneği)

	K2wr	K3wr	K4wr	K6wr	K8wr	K9wr	K1s	K7s
Al	4500	4400	3900	7200	6400	7400	34600	57400
Sb	0,18	0,47	0,29	0,16	0,33	0,25	1,61	1,05
As	1,3	2,5	2	1	1,4	3,9	12,6	13,5
Cu	3,2	2,6	3,3	2,4	3,1	4,8	14	17,1
Ba	90	20	170	220	40	270	230	310
Hg	<0,01	<0,01	<0,01	0,01	<0,1	<0,01	0,03	<0,1
Zn	2	4	<2	<2	2	<2	36	46
Fe	4000	9200	6400	3600	5400	7600	31100	36900
Ag	0,03	0,06	0,05	0,04	0,03	0,04	0,11	0,09
Cd	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	0,09	0,03
Cr	18	33	23	26	20	31	112	89
Co	0,6	0,4	0,3	0,8	0,6	0,9	18,3	21
Pb	2,1	2,2	2,8	2,1	2,2	3,7	27,5	22,3
Mn	39	31	37	53	50	56	889	541
Mo	0,87	1,56	1,67	1,53	0,94	1,56	1,89	1,71
Ni	2	2,5	1,7	2	1,9	2,8	24,3	34,8
Se	1	1	1	1	1	1	2	2
U	0,3	0,3	0,2	0,3	0,3	0,3	2,4	2,4

Table 7. The results of heavy metal analysis of spring water which sampled from the 2nd well of Kuvars Water (ppb)

Çizelge 7. Kuvars Su'ya ait 2 nolu kuyudan alınan kaynak suyunun ağır metal analiz sonuçları (ppb)

	September 2009	December 2009
Al^{3+}	32,3	96
Sb^{3+}	<0,1	<0,1
As^{3+}	0,15	0,16
Ba^{2+}	26,8	29,1
B^{3+}	<10	10
Cd^{2+}	<0,05	<0,05
Cr^{3+}	<0,5	<0,5
Co^{2+}	<0,1	0,11
Cu^{2+}	1,93	4,2
Fe^{2+}	38	96
Pb^{2+}	0,184	0,345
Mn^{2+}	1,97	2,02
Mo^{6+}	<0,05	<0,05
Hg^{2+}	<0,05	<0,05
Ni^{2+}	0,57	0,65
Se^{2-}	<1	<1
Ag^{+}	0,015	<0,010
U^{6+}	<0,010	<0,010
Zn^{2+}	8,8	12,5

RESULTS AND RECOMMENDATIONS

In 2011, the label informations from 53 companies producing bottled spring water in Istanbul are compared with the drinking and spring water limit values of WHO (2006), EPA (2009), CD (98/83/EC), TSE (2005) and Yönetmelik (2005). Some parameters on the 22 labels of 53 are exceeded the limits. The parameters exceeding the limits, are generally pH and SO_4 in waters from Çatalca, Mn and Cl in waters from Eyüp and Mn, pH and Cl in waters from Şile.

According to the geological settings of the production establishments of 53 spring water companies, 9 of the springs in Çatalca are emerging from metamorphic rocks, 4 of the springs in Şile are emerging from volcanic rocks, remaining 40 of the springs throughout the city are emerging from sedimentary rocks. The water companies are also generally located in forests, however 16 of them are close to urban areas.

Fe, Al, Mn ions, over the limit values in 9 springs of 40 where sedimentary rocks are aquifer, represent risk. It is considered that, concentrations of Fe, Al, Mn can be high in volcanics, because volcanic rocks have more trace elements than sedimentary rocks. Therefore, the companies procuring their spring waters from drill holes, should frequently analyse to confirm differences of heavy metal amounts in their waters. The companies should also avoid redudant well pumping in order not to cause heavy metal increases in their waters.

Some parameters in 9 of 16 springs which are close to urban areas are seen that they are over the limit values. It is known that the springs being too close to urban areas, especially, some antropogenic liquid waste could be mixed with shallow groundwater. Therefore, various organic materials and heavy metals that polluted in these groundwaters could negatively affect the human health. Bottled spring water producers, by determining the places where no contamination risks exist, should dig their wells in those points for actuating spring waters which have convenient qualification for consumer health.

Because there are some differences in the drinking and spring water limit values and parameters of WHO (2006), EPA (2009), CD (98/83/EC), TSE (2005) and Yönetmelik (2005), consumers could have difficulty while evaluating the quality of water. Likewise, recommended limit values of Ba, Zn, Ag, Mo and U ions do not exist in The Regulation Concerning Water Intended for Human Consumption (Yönetmelik, 2005). However, waters including such ions whose amounts exceed the recommended limit values, could be detrimental to human health if they are consumed frequently in a long period of time (EPA, 2001). Consequently, to intended and to conserve the human health, new regulations must be legitimated for The Regulation Concerning Water Intended for Human Consumption (Yönetmelik, 2005).

Various parametric values on label informations of spring water producers in İstanbul are specified

such as '0', not defined (ND) or 'absent', hereby these data cannot be compared with drinking and spring water limit values. As a solution of this problem, the institutions which analyze spring waters would be better if they use numeric expression such as under dedection limit '<X mg/l', instead of the expressions like '0', not defined (ND) or 'absent'. Furthermore, such lots of labels of bottled water in Europe (Pehlivan, 2007), in the Our Country amounts of all major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^{2-}) should also have been displayed on the labels of spring waters. In addition, it is reccomended to express amounts of some heavy metals (As, Ag, Hg, Co, Cd, Cr, Pb, Cu, Se, Sb, Mo, U, Zn etc.) and types of aquifer on the labels in order to develop the consumption consciousness.

Detailed geological investigations in the drainage areas of Hisar and Kuvars Water and evaluations of the two springs shown that heavy metal concentrations exceeding the drinking water limit values and possibly having toxic effect are not detected. However, some secondary clay minerals such as chlorite, kaolinite, illite and various secondary Fe-oxide minerals like limonite occur in the weathering zones of sandstones and graywackes of the Trakya Formation which is the aquifer in Hisar Water drainage area. It has also been seen that some limonite occur in the fractures of the Aydos Formation which is the aquifer in Kuvars Water drainage area. Consequently, depending on seasonal variations possible mixing of some heavy metals such as Fe, Mn, Al in Hisar Water and Fe and Al in Kuvars Water from the rocks to the spring waters should be taken into consideration.

ÖZET

Bu çalışma, İstanbul'da üretilen ambalajlı (damacana, şişe vb.) kaynak sularının kalite yönünden incelenmesi ve tüketime uygunluğunun değerlendirmesi kapsamında hazırlanmıştır. Yapılan çalışmalarda, 2011 yılı içerisinde, İstanbul'da üretilen ve halkın tüketimine sunulan 53 farklı ambalajlı kaynak suyu olduğu belirlenmiştir. İstanbul'da bulunan kaynak sularının insan sağlığına etkisini değerlendirilebilmek için ambalajların üzerindeki etiket bilgileri dikkate alınmıştır. Etiketlerde yer alan gösterge parametreleri içme ve kaynak suyu limit değerleri [(WHO, 2006), (EPA, 2009), (EU, 1998), (TSE, 2005) ve (Yönetmelik, 2005)] ile karşılaştırıldığında, İstanbul'da, 2011 yılında, ambalajlı kaynak suyu üretimi yapan 53 firmanın 22'sinde Mn, Cl, SO_4, pH, Fe, Al ve NH_4 gibi bazı parametrelerin limit değerlerini aştığı görülmüştür.

Kaynak sularının beslenim alanları, İstanbul'un genel jeolojisi ve çevresel durumu ile birlikte değerlendirildiğinde, söz konusu kaynak sularından 40 tanesinin sedimenter, 9 tanesinin metamorfik, 4 tanesinin ise volkanik kayaçlarla etkileşimde olduğu belirlenmiştir. Bununla birlikte, beslenim alanlarının çoğunlukla ormanlık alanlar içerisinde yer aldığı, ancak 16 tanesinde ise bazı yerleşim alanlarının bulunduğu görülmüştür. Genel bir yaklaşımla, metamorfik kayaçlarla etkileşimi olan Çatalca'nın kaynak sularında pH ve SO_4'ın, sedimenter kayaçlarla etkileşimi olan Eyüp'ün kaynak sularında Mn ve Cl'ün, Şile'nin kaynak sularında ise Mn, pH ve Cl miktarlarının standart ve yönetmeliklerin müsaade ettiği içme ve kaynak suyu limit değerlerine göre yüksek olduğu söylenebilir. Şile ve Eyüp ilçelerindeki kaynak sularının bazılarında, pH ve Cl miktarlarının limit değerlerin dışında olması, kuyuların, yüzey ve sığ yeraltı sularından etkilendiğine de işaret etmektedir.

Yapılan değerlendirmelerde, İstanbul'da, yaygın olarak sedimenter kayaçlardan kaynak suyunun sağlandığı ve yine en çok bu sularda limit değerleri aşan parametrelerin olduğu görülmüştür. Bu nedenle, Trakya ve Aydos Formasyonları gibi sedimenter kayaçların akifer olduğu, Kemerburgaz'daki Hisar Su ile Maltepe'deki Kuvars Su firmalarının kaynak sularının drenaj alanlarında jeolojik ve hidrojeokimyasal çalışmalar yapılarak, kaynak sularının sedi-

menter kayaçlarla olan etkileşimini incelenmiştir. Bu incelemeler kapsamında, söz konusu drenaj alanlarının 1/10000 ölçekli jeoloji haritaları hazırlanmış, arazilerden kayaç ve toprak örnekleri ile kaynak sularının çıkarıldığı su kuyularından Eylül 2009 ve Aralık 2009 dönemlerinde su örnekleri alınmıştır. Kayaç ve toprak örneklerinin iz element (Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Mo, Zn, Cu, Se, Sb ve U) analizleri ile kaynak sularının ağır metal (Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Mo, Zn, Cu, Se, Sb, B ve U) analizleri ALS Chemex (İzmir) Laboratuvarı'nda yaptırılmıştır.

Her iki kaynak suyunda da ulusal ve uluslararası içme suyu limit değerlerini aşan ve toksik etkisi olabilecek ağır metal belirlenmemiştir. Ancak; Hisar Su'yun akiferi Trakya Formasyonu'nun ayrışmış kumtaşı ve grovak seviyelerine bağlı olarak Fe, Mn, Al gibi iyonlar dönemsel olarak suda zenginleşme gösterebilir. Benzer bir şekilde, Kuvars Su'yun akiferi Aydos Formasyon'unun kuvarsarenitlerindeki limonitli ve killi sevileyelere bağlı olarak da Al ve Fe gibi iyonların suda artış göstererek su kalitesini olumsuz yönde etkileyebileceği dikkate alınmalıdır. Söz konusu riskin, aynı akiferlerden kaynak suyunu sağlayan diğer firmalar için de geçerli olabileceği düşünülmelidir. Ayrıca; beslenim alanlarında, volkanik, metamorfik veya cevher içeren çeşitli kayaçların mostra verdiği kaynak sularında da benzer araştırmaların yapılması halk sağlığı adına önem taşımaktadır.

Tüketicinin korunması ve bilinçlenmesi için kaynak sularındaki tüm ana iyon ve toksik etkisi olan tüm ağır metal miktarlarına ambalajlı suların etiket bilgilerinde yer verilmelidir. Bu nedenle, İnsani Tüketim Amaçlı Sular Hakkındaki Yönetmelik'te (Yönetmelik, 2005) bazı düzenlemelerin yapılması gereği vardır.

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