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WATER QUALITY AND PROTECTION: ENVIRONMENTAL ASPECTS

Observation of Excess Heavy Metal Concentrations in Water Resources to Infer Surface Water Influences on Shallow Groundwater: a Typical Example of the Porsuk River (Eskisehir-Turkey)[1]

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Abstract—The Eskisehir province is well-known due to its industrial and agricultural activities, which are a threat for the aquatic environment. Hence, monitoring of water quality in the area is of vital importance because of an excess heavy metal contents, especially As. The Porsuk River is heavily polluted by industrial activities from Kutahya city. It discharges into the Porsuk Dam and from there it flows relatively clean to Eskisehir city center, but beyond this point it increasingly deteriorates due to the negative impact of industrial and agricultural activities up to the junction point of Porsuk and Sakarya rivers. Heavy metal concentrations and As contents in surface and ground waters were selected as pollution indicators to examine pollution level and compare an interaction between river and groundwater. For this purpose, water samples taken between 2008 and 2010 from the Porsuk River along the section from the west of Kutahya to the discharge point into the Sakarya River, as well as groundwater samples from the wells located close to or far of the Porsuk River, were evaluated. Based on the obtained results, we found that the Porsuk River, especially at the locations close to the Sakarya River, and groundwater are polluted in terms of heavy metals and As compounds. In conclusion, the heavy metal and As pollution is also observed in the wells close to the locations in which groundwater is fed by the Porsuk River since it acts as an influent river. Thus, surface water is considered as a polluting source of groundwater.

Keywords: Porsuk River, groundwater, pollution, heavy metal, arsenic

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INTRODUCTION

The study area is occupied about 500 km^2 in the north-western part of Middle Anatolia between 39°41′00″–39°32′30″ N and 30°22′46″–31°08′00″ E including the city of Eskisehir (Fig. 1) [10]. The total length of the Porsuk River is 436 km with the area of 11 326 km^2 [1]. In recent years, the Porsuk River which has been widely used for domestic water supply is increasingly polluted in terms of heavy metals, especially As. In spite of the water treatment plant for the Porsuk River, the increase in urban population, the intense activities of the various branches of industry, uncontrolled discharges of chemical wastes are the major causes of this pollution [3, 10]. Water samples, especially taken from the Porsuk River at Eskisehir sugar mill and the wastewater treatment plant after 2001, had the reduction in the value of dissolved oxygen and an increase in the chemical and biological oxygen requirement indicate that pollution is increasing [11].

This study aims to investigate the pollution of surface water caused by the waste generated by industrial and agricultural activities along the river catchment, as well as the pollution occurred in groundwater because of the river influence, since the river passes through the center of the city and carries the waste water into groundwater. As a result, the pollution of the groundwater was identified with their possible sources.

MATERIALS AND METHODS

Study Area and Geology

Triassic metamorphic schist-marble and ophiolitic melange is the oldest units in the study area [5]. Eocene, Early and Middle Miocene age formations are unconformably overlain by the Pliocene age series mainly composed of conglomerate and sandstone, agglomerate, tuff-tuffite, basalt-andesite, and marl-

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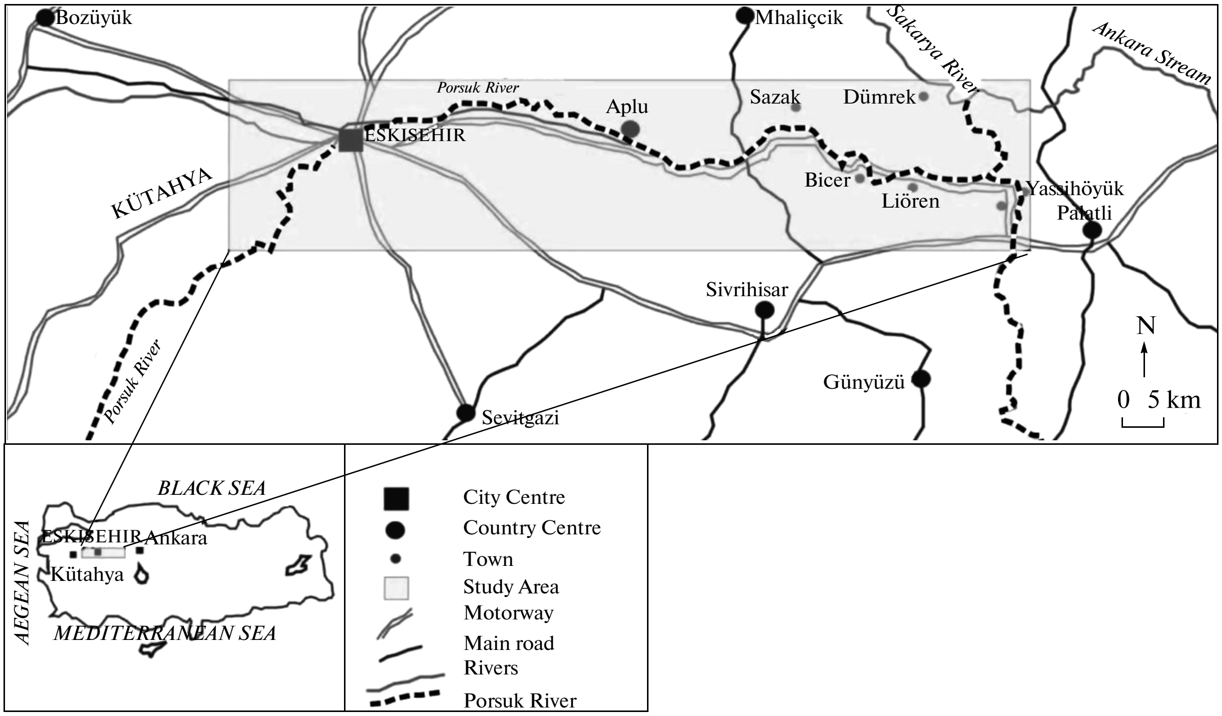

Fig. 1. Location map of the study area.

claystone (Fig. 2). The alluvium composes of two parts of Pleistocene age (Villafransiyen) and Late Quaternary deposits which were cut by all drilled wells in the study area. Alluvium is an essential aquifer mainly composed of the gravel, sand and silt materials [2]. The total thickness of old and young alluvium reaches up to 120 m. However, the thickness of young alluvium varies between 10 and 15 m. The study area is defined as a graben basin formed in the late Neogene with strike-slip faults and thrust faults developed in the east-west direction, due to the pressures in the north-south direction started at the end of the Triassic period [2]. Figure 3 shows the general groundwater direction along the Porsuk River from east towards west.

Sample Collection and Extraction Procedures

35 samples of the ground water and 38 samples of the surface water were taken within the scope of this study to investigate the relationship between pollution parameters and surface water-groundwater interaction on the basis of the Porsuk River. Sampling information is given in Table 1. A Garmin brand handheld GPS was used to transfer the sampling points to the map. Plastic bottles of 1 L were used for sample collection. The water samples for heavy metal analysis were filtered through 0.45 μm PTFE (polytetrafluoroethylene) syringe filter. After filtration diluted HNO_3 (5% N) was added to ensure the pH ≤ 2 conditions. Metal compounds were prevented to form complex compounds with oxygen. Heavy metal analysis was performed by the EPA 200.8 method through "ICP_MS" device in the local laboratory of the State Hydraulic Works (DSI). By the EPA 200.8, heavy metal contents in question, including As, were ionized in ICP by argon before introducing into the MS. Thus, they were quantified by considering their mass/charge ratio. Detection limit and uncertainty were 0.20 μg/L (LOD) and 0.07 μg/L, respectively. The analytical results were given in Tables 2 and 3. The acceptability of the heavy metal contents of the groundwater and surface water samples according to Turkish Drinking Water Standards [6] were examined. Obtained results were plotted and evaluated in graphs to understand possible relations between surface water and groundwater interaction. Distribution of As, Zh, Fe, Mn and Ni in water samples was plotted on the maps by Surfer program using Krigging approach.

RESULTS AND DISCUSSION

The analytical results of the heavy metals, and As were evaluated over the data on all groundwater (Table 2) and surface water (Table 3) samples collected in this study. All sampling points were plotted onto the map to better understand their interactive distances between surface and groundwater samples (Fig. 4). The heavy metal, and As correlation tables of the groundwater and surface water in 2008–2010, and the correlation coefficients of the groundwater and surface water samples were investigated considering their close proximity to each other. Finally the plots of the

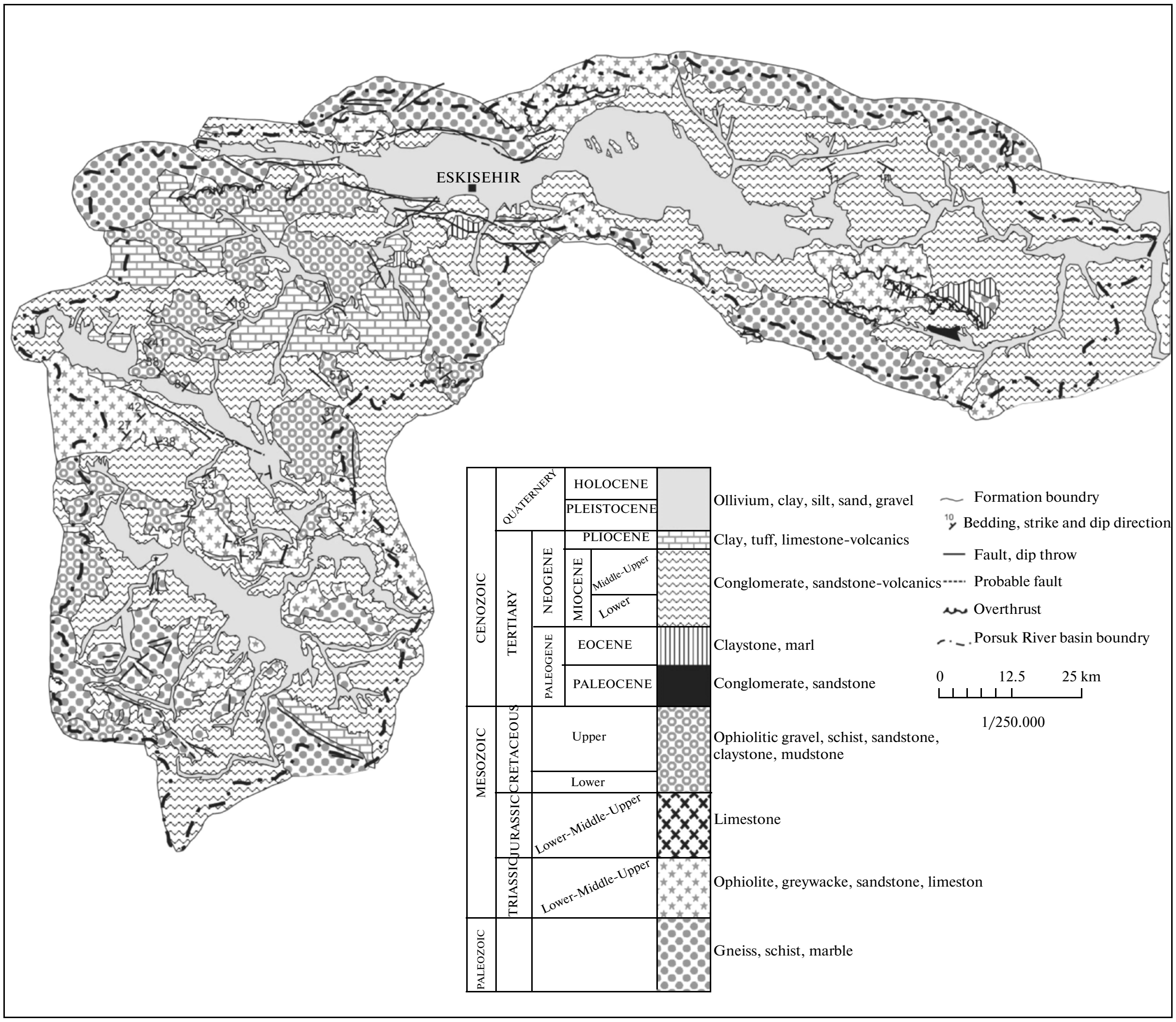

Fig. 2. Geology map of the study area.

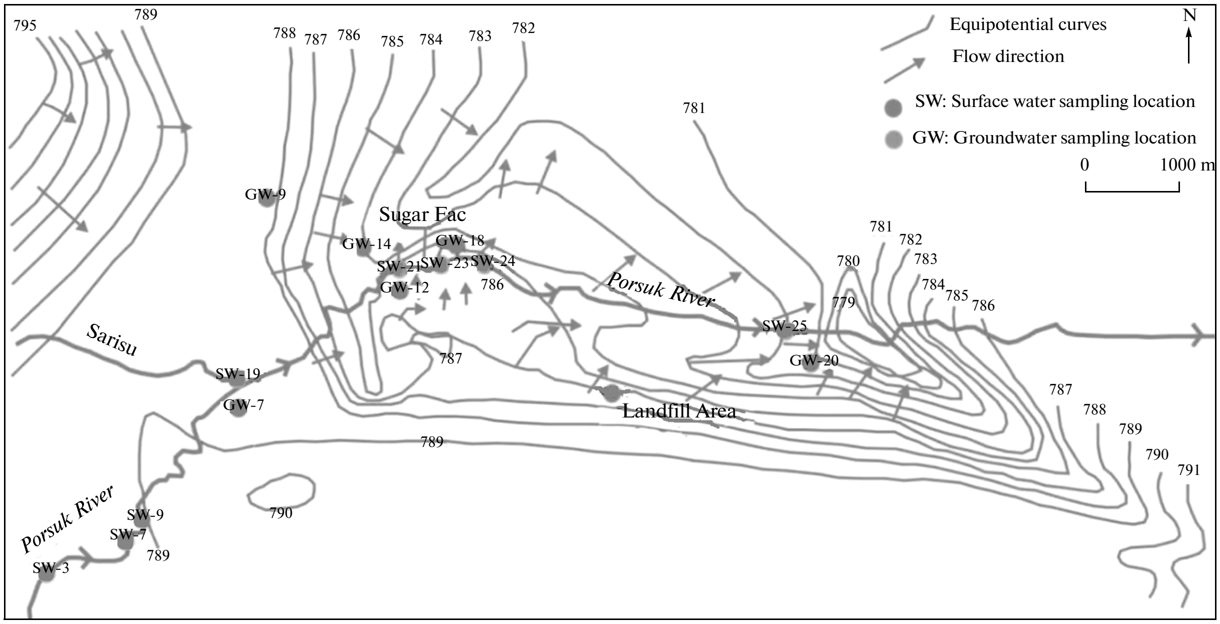

Fig. 3. Groundwater equipotential lines and flow directions (after [10]).

Table 1. The information of groundwater and surface water sampling locations

Sample No	Location Name	Sample No	Location Name
GW-1	Behind the flour mill Kızılinler	SW-1	Kutahya before purification
GW-2	Yusuflar village	SW-2	Kutahya after purification
GW-3	Karacasehir Rural Services well (47076)	SW-3	Agaçkoy
GW-4	Eskisehir entry from Kutahya	SW-4	Kutahya before nitrogen factory
GW-5	Garbage dump site	SW-5	Kutahya after nitrogen factory
GW-6	17147 numbered well	SW-6	Calca Before joint of Porsuk River and
GW-7	31969 numbered Sarar (Sumerbank) well	SW-7	Guvez Stream
GW-8	Source in garbage dump site estuary	SW-8	Bridge of Guvez Stream after joint Porsuk River and Guvez
GW-9	43036 numbered State Supply Office well	SW-9	Stream
GW-10	14768 numbered Anadolu University (Academy) well	SW-10	Sabuncupinar Bridge
GW-11	DSI well	SW-11	Sabuncupinar Stream Kargin
GW-12	Suleyman Cakir (Justice Elementary School) well	SW-12	Porsuk Dam exit
GW-13	A dig well in garbage dump site	SW-13	Ulucayir Stream
GW-14	38673 numbered Tulomsas well	SW-14	Esenkara 1
GW-15	TSK–13 numbered well	SW-15	Porsuk River after Kizilinler village
GW-16	Sugar factory well	SW-16	Forest nursery at city entrance
GW-17	Sugar factory well	SW-17	Before Porsuk River purification
GW-18	Sugar factory wells	SW-18	Front of Sümerbank factory
GW-19	DSI 3. Region Machine supply well	SW-19	Sarisu Channel
GW-20	32996 numbered Tusas well	SW-20	Adalar entrance (Ataturk street bridge)
GW-21	5779/B slaughter house well	SW-21	Çukurcarsi
GW-22	Elementary school well	SW-22	Before Sugar factory
GW-23	46169 numbered SSK Maternity Hospital well	SW-23	After Sugar factory
GW-24	1047 Muttalip well	SW-24	After slaughter house
GW-25	30177 Numbered Meat and Fish Authority well	SW-25	Porsuk River air base
GW-26	Organized Industry well (no. 10)	SW-26	City exit (Hasan Bey farm bridge)
GW-27	A shallow well (10 m depth)	SW-27	Irrigation Channel 1
GW-28	South of PC/VIII numbered well	SW-28	Irrigation Channel 2
GW-29	39345 numbered Botas well	SW-29	Alpu
GW-30	50 m depth well in Catma Farm	SW-30	Beylikova
GW-31	Drilling well at Alpu exit	SW-31	Yunusemre
GW-32	Shallow well at Beylikova exit	SW-32	Bicer village Porsuk River
GW-33	Shallow well of Yunusemre Municipality	SW-33	Iloren-Sazilar
GW-34	A well in the Bicer village	SW-34	Sakarya River before Porsuk River before joint of Porsuk River and
GW-35	A well in the Kiranharmani village	SW-35	Sakarya River
SW-36	After joint of Porsuk River and Sakarya River		
SW-37	Ankara Stream		
SW-38	Before joint of Ankara Stream Sakarya River		

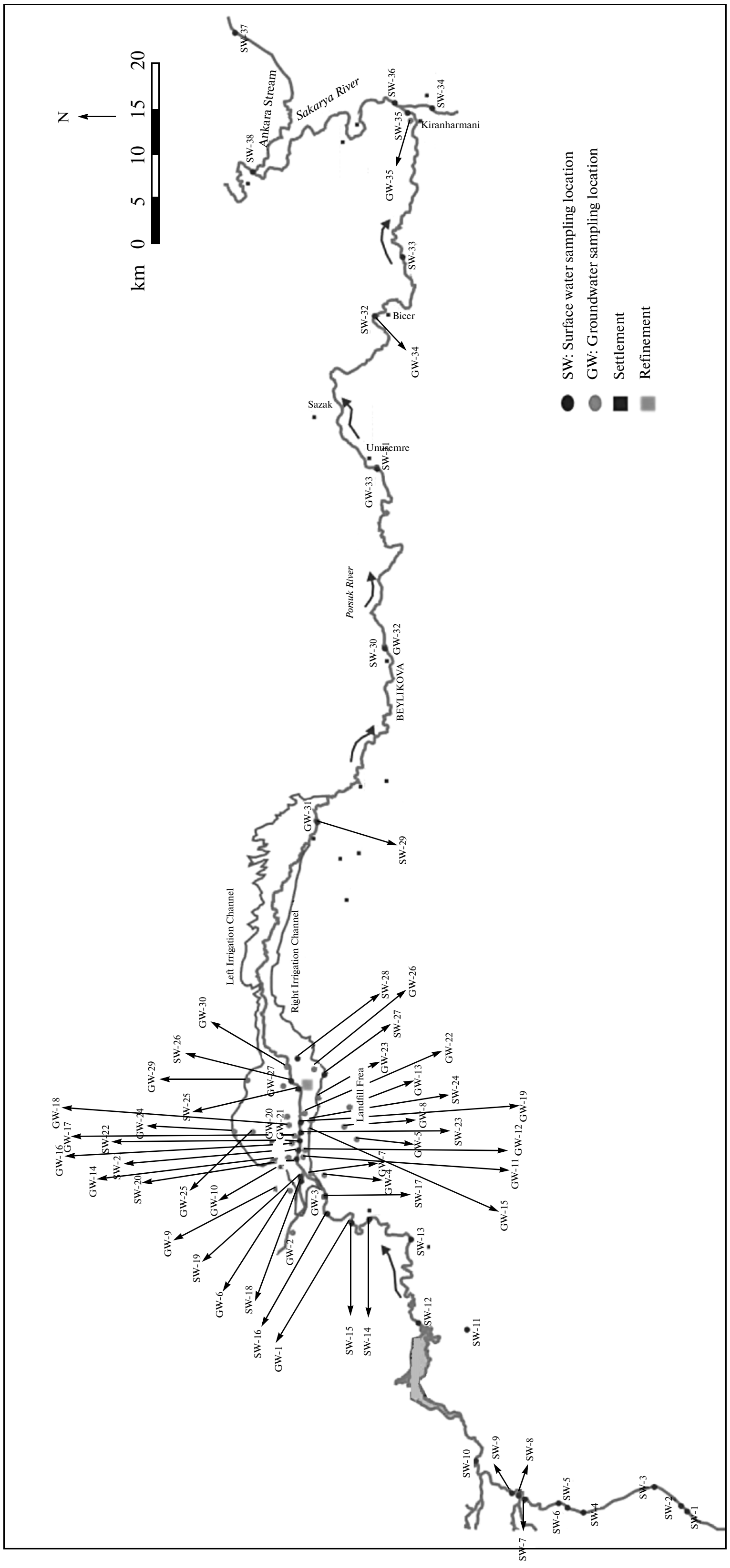

Fig. 4. Ground water and surface water sampling locations in the study area.

Table 2. Heavy metal analyses results which belong to groundwater between 2008 and 2010, the bold values indicate over limit according to the [4] (GW: Groundwater sample, W: Wet period, D: Dry period)

Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As	Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As
ITASHY (2005)		*10*	*100*	*50*	*50*	*200*	*200*	*20*	*200*	*10*	±	ITASHY (2005)		*10*	*100*	*50*	*50*	*200*	*200*	*20*	*200*	*10*	±
GW-1	2010 W		95.35	6.92						**11.57**	0.81	GW-18	2008 D	0.20		9.78	**413.00**	14.17	1.32	16.76	5.67	**24.40**	1.71
GW-1	2010 D	3.49	**142.70**	13.81			4.64			**12.12**	0.85	GW-18	2009 W	0.67	0.00	5.08			0.00			**28.33**	1.98
GW-2	2008 D	2.23		7.22	6.74	182.50	0.00	5.07	5.92	1.12	0.08	GW-18	2009 D		5.29				3.23			**19.01**	1.33
GW-7	2008 W	0.00		8.06	0.00	17.98	0.00	0.00	0.00	**10.17**	0.71	GW-18	2010 W		6.98	7.60			8.22			**21.56**	1.51
GW-7	2008 D	0.26		18.09	2.39	145.80	1.42	0.73	3.76	**15.12**	1.06	GW-18	2010 D		14.57	13.28			7.71			**22.21**	1.55
GW-7	2009 W	0.09	0.00	8.85			0.00			**13.48**	0.94	GW-21	2009 W	0.00	0.00	1.07			0.00			3.79	0.27
GW-7	2009 D	0.78	**505.70**	6.37			2.94			**12.73**	0.89	GW-21	2009 D		136.90	11.06			3.21			5.55	0.39
GW-7	2010 W		17.28	11.06						**10.98**	0.77	GW-21	2010 W			2.84						3.16	0.22
GW-7	2010 D	**10.35**	15.01							**12.40**	0.87	GW-21	2010 D		**103.70**	47.92			4.82			6.96	0.49
GW-8	2009 W	0.00	0.00	21.54			0.00			1.55	0.11	GW-22	2008 W	1.74		1.13	**21.62**	**649.30**	3.70	2.58	0.07	1.32	0.09
GW-8	2009 D			17.16						1.78	0.12	GW-22	2008 D	0.20		8.17	**62.90**	**338.70**	3.46	4.19	15.68	1.22	0.09
GW-8	2010 W		6.37	27.65			15.16			2.29	0.16	GW-22	2009 W	0.25	**101.80**	1.65			0.00			0.91	0.06
GW-8	2010 D			26.79						2.08	0.15	GW-22	2009 D		**207.50**				5.37			1.22	0.09
GW-9	2008 W	0.00		11.41	1.24	**356.70**	0.00	5.33	0.00	1.60	0.11	GW-22	2010 W		**141.50**	4.65			3.91			0.95	0.07
GW-9	2008 D	2.31		7.24	7.39	**200.00**	3.49	5.47	26.84	1.12	0.08	GW-22	2010 D		23.80	9.61			6.77			2.48	0.17
GW-9	2009 W	0.00	0.00	1.15			0.00			3.80	0.27	GW-26	2008 W	0.00		8.47	0.29	50.04	0.00	0.29	0.05	2.15	0.15
GW-9	2009 D		82.48	2.98						1.34	0.09	GW-26	2008 D	**10.11**		13.42	1.16	125.90	**198.00**	2.96	15.66	3.06	0.21
GW-9	2010 W		60.98	10.00						1.14	0.08	GW-26	2009 W	1.14	0.00	3.03			0.00			**14.30**	1.00
GW-9	2010 D	0.60	**641.10**	8.13			5.48			1.47	0.10	GW-26	2009 D		32.37	2.59			2.23			**12.30**	0.86
GW-10	2008 W	0.00		14.64	0.00	43.99	0.00	4.21	0.24	3.08	0.22	GW-26	2010 W			14.61						**13.77**	0.96
GW-10	2008 D	0.36		19.26	0.87	16.71	2.51	5.73	2.33	4.31	0.30	GW-26	2010 D		10.48	15.73						9.75	0.68
GW-12	2008 W	0.00		4.55	1.94	97.68	0.08	16.53	0.37	**27.44**	1.92	GW-30	2008 W	0.00		7.49	3.02	174.70	0.00	2.15	0.15	6.92	0.48
GW-12	2008 D	0.96		12.19	3.03	117.00	1.60	9.46	2.80	**38.74**	2.71	GW-30	2008 D	0.30		14.57	4.40	122.00	0.49	2.33	18.70	9.80	0.69
GW-12	2009 W	0.79	32.01	8.01			0.00			**33.53**	2.35	GW-30	2009 W	0.16	0.00	9.92			0.00			8.32	0.58
GW-12	2009 D		**517.00**							2.09	0.15	GW-30	2009 D		24.89	1.95						**10.11**	0.71
GW-12	2010 W		**721.70**	2.22						2.52	0.18	GW-30	2010 W		16.48	16.35			3.62			**11.17**	0.78
GW-12	2010 D	1.93	**181.20**	11.82			10.65			**35.77**	2.5	GW-30	2010 D			13.57						8.29	0.58
GW-13	2008 W	0.00		20.23	0.00	26.10	0.00	0.88	0.13	1.23	0.09	GW-31	2010 W			5.44			2.79			**11.68**	0.82
GW-13	2008 D	0.59		24.80	0.68	16.74	0.99	1.73	7.39	1.64	0.11	GW-31	2010 D		9.41	6.63						**41.01**	2.87
GW-13	2010 D											GW-32	2010 W		4.62	25.17			5.17			9.86	0.69
GW-14	2008 W	0.00		6.76	0.13	108.40	0.00	8.14	0.00	9.59	0.67	GW-32	2010 D	**11.92**	28.65	29.08			40.7			10.85	0.76
GW-14	2008 D	0.17		12.01	**99.26**	28.94	0.22	8.00	0.00	**11.41**	0.80	GW-33	2010 W			91.82			3.37			**36.1**	2.53
GW-14	2009 W	0.00	0.00	8.41			0.00			9.48	0.66	GW-33	2010 D	0.44	20.39	8.32			7.03			**10.84**	0.76
GW-14	2009 D			4.07						8.35	0.58	GW-34	2010 W	0.95	27.58	4.67			33.79			**40.45**	2.83
GW-14	2010 W			10.14			6.91			9.97	0.70	GW-34	2010 D	0.52	23.05	9.78			7.86			**11.41**	0.80
GW-18	2008 W	0.83		0.59	**466.80**	**523.60**	12.31	**22.67**	0.13	**13.17**	0.92	GW-35	2010 W	6.51	39.79	14			95.59			8.08	0.57

Table 3. Heavy metal analyses results which belong to surface water between 2008 and 2010, the bold values indicate over limit according to [4] (GW: Groundwater sample, W: Wet period, D: Dry period)

Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As	Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As
ITASHY (2005)		10	100	50	20	50	100	20	200	10	±	ITASHY (2005)		10	100	50	20	50	100	20	200	10	±
A1	2008 W	0.73		0.97	3.03	**107.2**	8.31	2.61	69.6	1.85	0.13	SW-23	2010 W		4.90	6.24						**13.28**	0.93
A1	2008 D	0.45		5.51	2.2	41.99	1.61	6.14	**221.3**	**11.35**	0.79	SW-23	2010 D		12.60	5.47			5.28			**11.92**	0.83
A1	2009 W	1.05	**151.3**	1.05			0			3.76	0.26	SW-24	2008 W	1.55		4.50	**85.06**	**137.00**	0.00	8.01	**347.90**	**9.75**	0.68
A1	2009 D		60.83							5.39	0.38	SW-24	2008 D	1.61		6.27	**56.15**	**215.90**	0.00	9.17	82.02	**16.25**	1.14
A1	2010 W		68.09	2.94						3.29	0.23	SW-24	2009 W	0.70	0.00	5.81			0.00			8.74	0.61
A1	2010 D		20.94	4.37			4.4			8.69	0.61	SW-24	2009 D									**10.43**	0.73
SW-7	2009 D	**61.22**	**153.20**	5.44						**14.24**	1.00	SW-24	2010 W	3.86	36.72	8.36			34.39			**13.45**	0.94
SW-7	2010 W	**113.50**	53.99	8.52			18.03			**13.92**	0.97	SW-24	2010 D		13.43	5.57			4.81			**11.18**	0.78
SW-7	2010 D	**23.05**	84.07	7.34			21.80			**13.01**	0.91	SW-25	2008 W	2.03		6.02	**134.10**	**421.10**	2.26	**23.56**	**502.10**	**10.92**	0.76
SW-8	2009 D			4.66						4.11	0.29	SW-25	2008 D	5.19		14.16	**177.30**	**3084.00**	10.19	**53.33**	**219.20**	**12.06**	0.84
SW-8	2010 W	3.71	44.34	22.25			31.02			**10.25**	0.72	SW-25	2009 W	3.22	**243.60**	10.55			0.00			6.91	0.48
SW-8	2010 D	0.73	31.46	11.25			6.74			5.47	0.38	SW-25	2009 D	7.37	**329.00**	10.63			**100.20**			**9.78**	0.68
											1.08												0.34

Table 3. (Contd.)

Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As	Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As
SW-9	2009 D	**96.71**	**224.90**	10.54			15.16			**15.39**	± 0.90	SW-25	2010 W	7.71	**207.80**	14.69			19.78			4.86	± 0.73
SW-9	2010 W	**58.08**	43.00	4.75						**12.85**	0.93	SW-25	2010 D	2.69	**184.90**	14.20			17.30			**10.47**	0.20
SW-9	2010 D	**13.04**	55.07	5.88			6.73			**13.32**	0.87	SW-29	2010 W	6.20	**231.80**	18.27			13.65			2.83	0.57
SW-15	2010 W	1.24	10.30	3.84			19.24			**12.37**	0.85	SW-29	2010 D	2.82	35.36	9.97			9.92			8.13	0.47
SW-15	2010 D		9.09	4.71			4.17			**12.13**	0.58	SW-30	2010 W	2.27	41.30	10.23			13.04			6.65	0.61
SW-17	2008 W	0.37		0.70	**31.87**	**79.99**	0.00	3.87	71.46	8.27	1.16	SW-30	2010 D	4.37	90.01	15.56			12.38			8.68	0.88
SW-17	2008 D	0.93		4.92	**41.91**	**149.40**	1.95	6.70	25.91	**16.62**	0.90	SW-31	2010 W	1.57	11.49	7.04			16.13			**12.55**	0.67
SW-17	2009 W	0.69	0.00	2.92			0.00			**12.84**	1.00	SW-31	2010 D	1.20	32.25	10.53			8.34			9.59	1.13
SW-17	2009 D	1.75	32.95				116.00			**14.29**	0.88	SW-32	2010 W			7.70			3.83			**16.21**	0.81
SW-17	2010 W	1.58	10.89	3.83			20.42			**12.60**	0.82	SW-32	2010 D	1.61	32.70	13.34			8.87			**11.51**	1.45
SW-17	2010 D		9.43	4.69			3.55			**11.70**	0.44	SW-34	2010 W	1.43	19.81	5.61			21.39			**20.66**	0.99
SW-19	2008 W	0.00		1.51	**58.15**	**198.40**	0.00	8.82	170.10	6.35	0.74	SW-34	2010 D	0.71	14.09	7.68			7.10			**14.13**	1.56
SW-19	2008 D	0.82		8.08	**24.82**	**229.50**	0.36	9.60	193.00	**10.62**	0.60	SW-SW-35	2009 D			3.87						**22.24**	2.14

Table 3. (Contd.)

Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As	Sample No	Year	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	Mn (µg/L)	Fe (µg/L)	Cu (µg/L)	Ni (µg/L)	Al (µg/L)	As (µg/L)	Error margin for As
SW-19	2009 W	0.00	0.00	3.32			0.00			8.55	±	SW-35	2010 W	3.57	15.26	5.81			50.88			**30.64**	±
											0.44												1.05
SW-19	2009 D									6.29		SW-35	2010 K	1.21	24.52	10.97			11.68			**14.98**	
											0.53												1.09
SW-19	2010 W		16.63	5.36						7.64		SW-36	2009 D			3.77						**15.62**	
											0.58												1.50
SW-19	2010 D		9.23	4.82			3.79			8.31		SW-36	2010 W		7.60	6.54			8.86			**21.44**	
											0.58												0.96
SW-21	2008 W	0.00		7.22	**26.23**	**59.60**	0.00	3.75	**238.10**	8.25		SW-36	2010 D	0.59	18.33	6.42			8.87			**13.71**	
											1.17												1.30
SW-21	2008 D	0.64		7.16	**26.76**	**131.70**	0.18	6.62	170.30	**16.66**		SW-37	2009 D	8.49	**116.40**	21.24			7.10			**18.55**	
											0.48												0.93
SW-21	2009 W	1.02	5.53	5.43			0.00			6.90		SW-37	2010 W	6.91	**130.40**	21.23			43.21			**13.25**	
											0.61												0.87
SW-21	2010 W	2.96	**600.20**	3.73			3.70			8.76		SW-37	2010 D	4.07	**106.70**	20.17			22.87			**12.38**	
											0.77												1.28
SW-21	2010 D	0.85	27.76	6.28			5.63			**10.97**		SW-38	2009 D	1.15	12.87	7.89						**18.25**	
											0.60												1.71
SW-23	2008 W	0.00		2.05	**28.92**	**60.05**	0.00	3.16	**281.80**	8.61		SW-38	2010 W	8.14	**131.8**	23.5			45.42			**24.47**	
											1.18												1.19
SW-23	2008 D	0.25		6.01	17.71	41.62	0.00	6.41	129.30	**16.86**		SW-38	2010 D	2.77	42.41	12.15			21.12			**17.02**	
SW-23	2009 W	0.06	0.00	4.84			0.00			**11.18**	0.78												

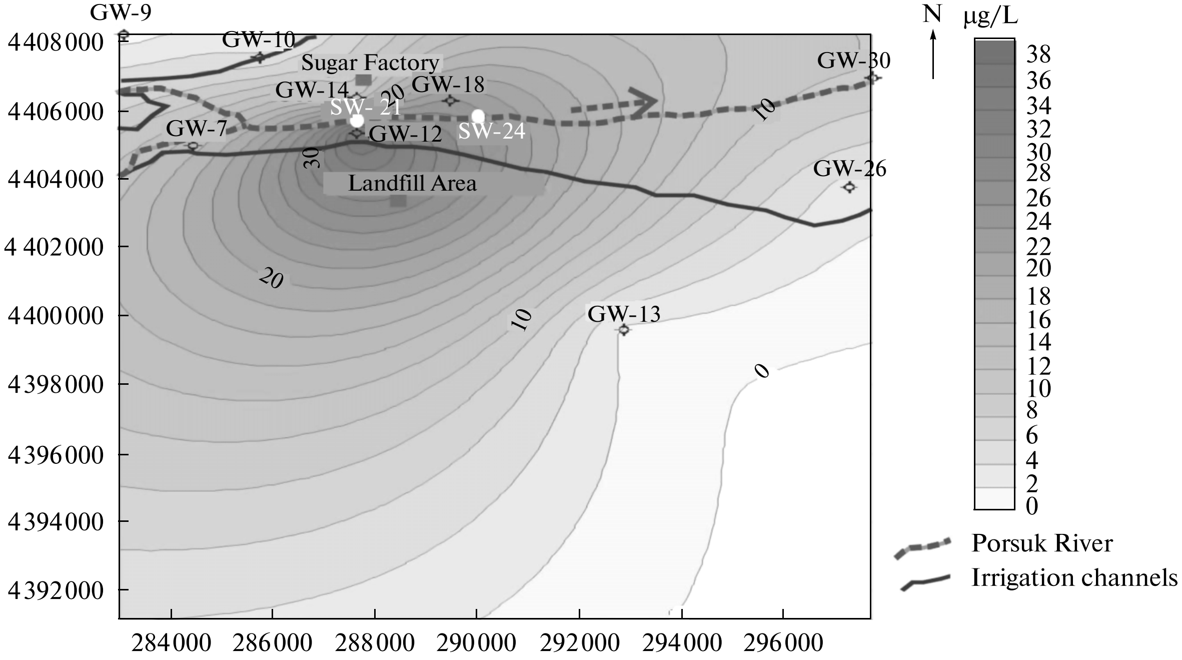

Fig. 5. As distribution map of the sampling locations in the dry period of 2008.

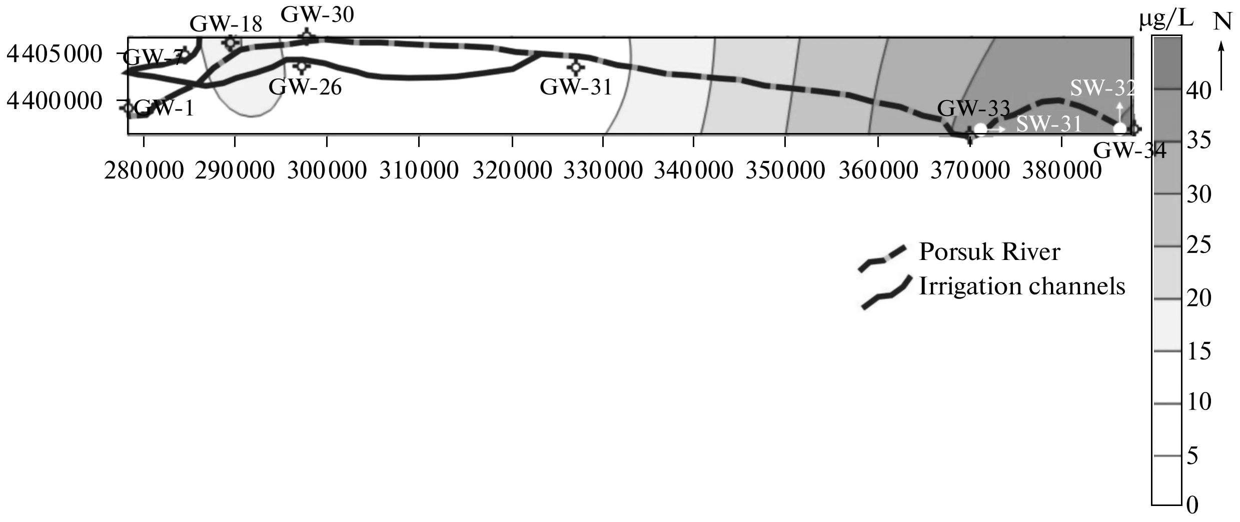

Fig. 6. As distribution map of the sampling locations in the dry period of 2010.

heavy metals contained in the groundwater samples were drawn according to the standards set by the TDWS [6], and the sampling points that exceed the limit values were identified.

The As, Fe, Ni, Mn and Zn distribution maps of the groundwater samples were plotted to assess if there was any interaction between groundwater and surface water (Figs. 5–13). Furthermore, similar interaction was searched by the evaluation of Tables 2 and 3. The evaluation of these maps revealed that the groundwater samples located close to the Porsuk River or irrigation canals have higher concentrations of heavy metals and As. It could be related to old fashion agricultural activities that used arsenical pesticides or surface water influence. Most possibly, high As content in groundwater in some parts of the study area is sourced from the remnants of arsenic based pesticides which accumulated at the top of soil and infiltrates into groundwater through irrigation waters.

Indeed, As content in all samples was less than 50 μg/L, which was the previous Maximum Contaminant Level (MCL). However, the Joint FAO/WHO

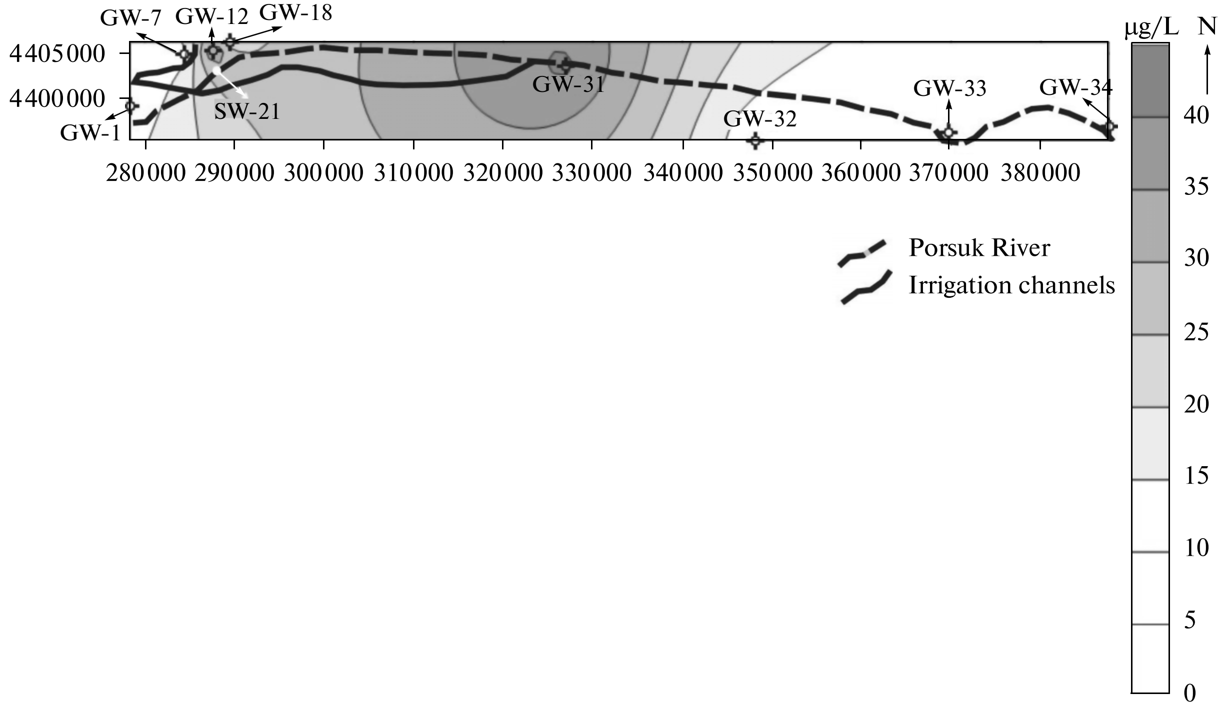

Fig. 7. As distribution map of the sampling locations in the dry period of 2010.

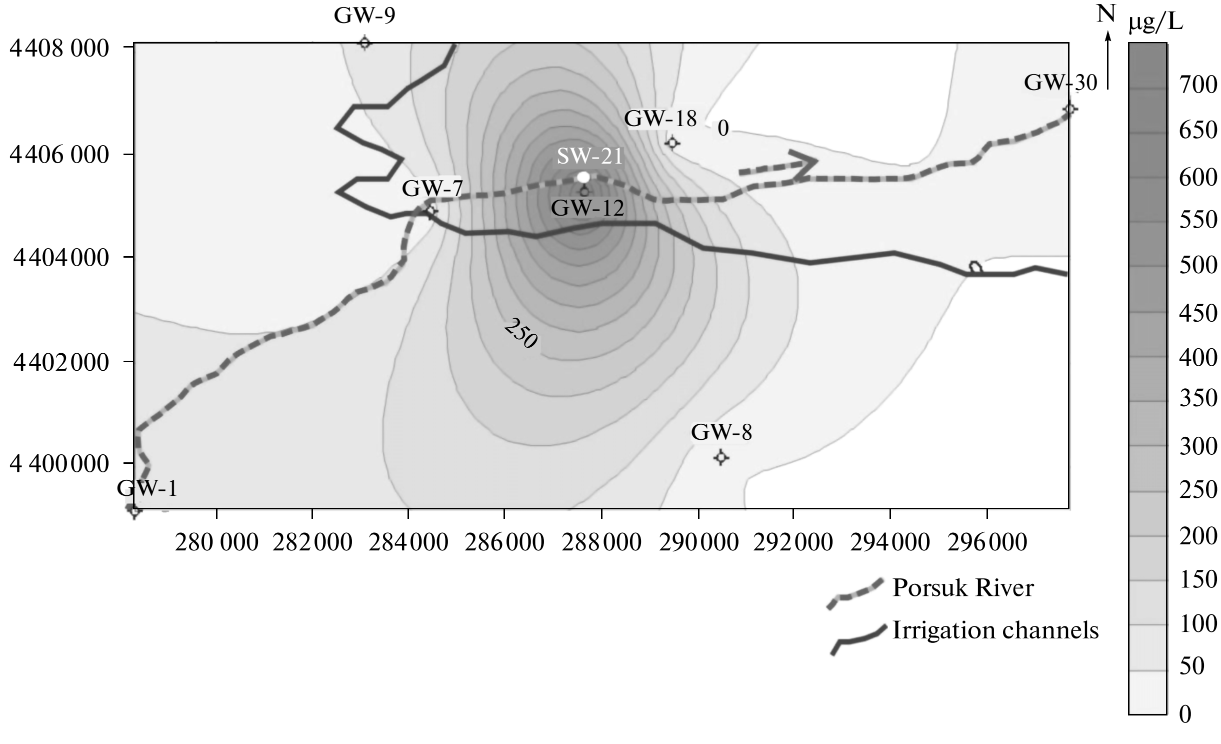

Fig. 8. Zn distribution map of the sampling locations in the dry period of 2010.

Expert Committee on Food Additives (JECFA) reassessed the effects of As on human health, taking into account the new data. Moreover, EPA requested from the National Academy of Sciences (NAS) to review the Agency's interpretation and application of As research, worked with its National Drinking Water

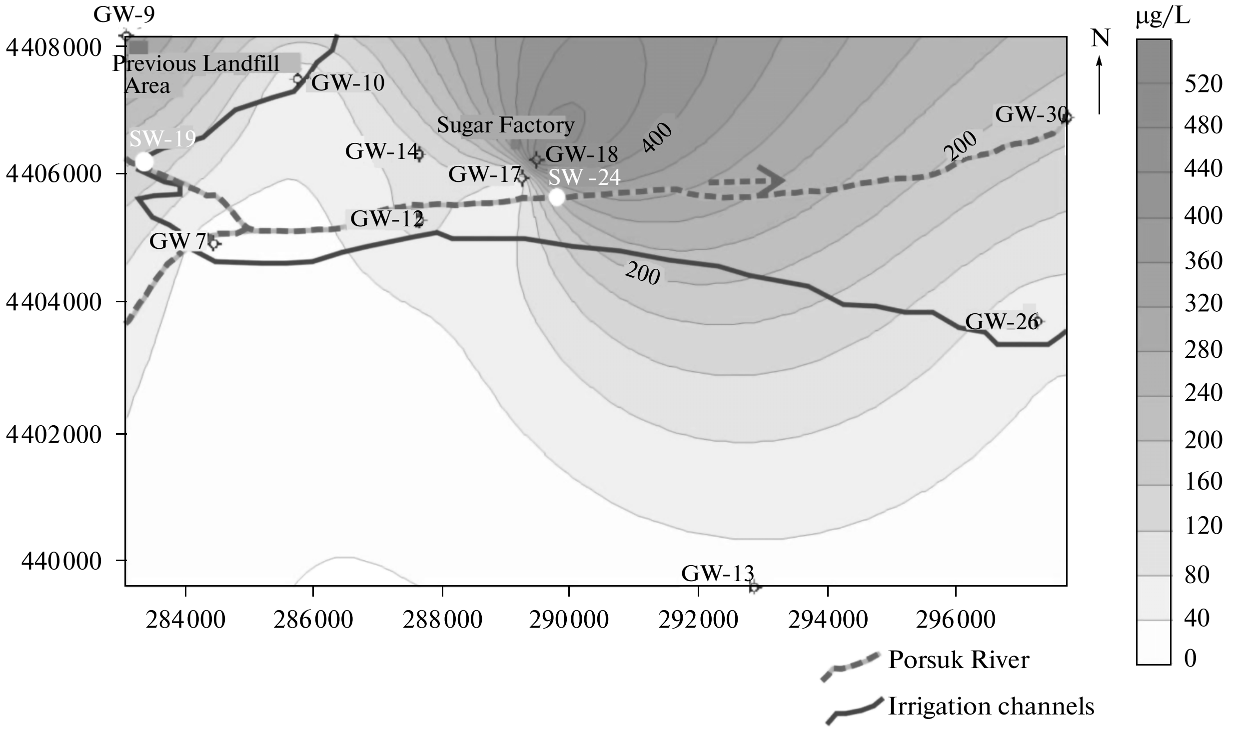

Fig. 9. Fe distribution map of the sampling locations in the dry period of 2008.

Advisory Council (NDWAC). Finally, the MCL was decreased to 10 μg/L after all these scientific research and discussions. In spite of the unfavorable consequences that may come from moderately high levels of As in water (10–50 μg/L), the Committee stated that such intervals could be considered as tolerable [8]. In conclusion, EPA announced that 10 ppb (0.010 mg/L) standard for As would remain as an achievable limit for public health to protect probable unsatisfactory results.

As can be seen from the distribution of As in the dry period of 2008 (Fig. 5), As concentrations in SW-21 and GW-12 are 16.66 and 38.74 μg/L, respectively. Groundwater might be contaminated from Landfill Area (Fig. 3). On the other hand the As contamination of the groundwater from the Porsuk River is rejected for these couple (GW-12, SW-21) because the groundwater is discharged to the surface water where these samples are located (Fig. 3). Both values are clearly higher than the allowable limit for drinking water (10 μg/L) according to [6]. Since the position of SW-21 is very close to the GW-12, high As content in GW-12 most probably occurs due to surface water-groundwater influence between SW-21 and GW-12. A similar interaction can be expected between GW-18 and SW-24, which is nearby the GW-18 with a higher As concentration (16.25 μg/L).

The possible interaction can also be observed between SW-31 (12.55 μg/L), SW-32 (16.21 μg/L) and, GW-31 (11.68 μg/L), GW-33 (36.1 μg/L), GW-34 (40.45 μg/L) that are above the standard during the wet period of 2010 (Fig. 6). As concentration in GW-12 (35.77 μg/L) may also influenced by SW-21 (10.97 μg/L) during the dry period of 2010 (Fig. 7). However, relatively higher As contents in groundwater showed reverse migration, i.e., groundwater contaminates the Porsuk River. High As content in the groundwater samples relatively increase during dry period due to the lack of fresh water recharge, such as rainfall.

On the other hand, higher As concentrations in the samples taken in the vicinity of the confluence of Sakarya and Ankara streams (SW-35, SW-36, SW-37, and SW-38) (Fig. 4) are thought to be closely related to the geological units they are located on, their proximity to the intense industrial and agricultural areas, and returning irrigation water to the river.

The same influence can be found between GW-12 and SW-21 based on the Zn concentration for the wet period of 2010 (Fig. 8), since the Zn concentration is above the allowable limit of TDWS (100 μg/L) by 600.20 μg/L in SW-21 and 721.70 μg/L in GW-12 which are located close to each other.

The distribution of Fe during the wet period of 2008 is shown in Fig. 9. The Fe concentration in GW-9 and SW-19 are 356.70 and 198.40 μg/L, respectively that are above the allowable limit (50 μg/L) for drinking purpose. Hence, a probable groundwater-surface water interaction between GW-9 and SW-19 can be implied. Furthermore, Fe concentration in SW-21 (131.70 μg/L) is comparable with GW-12

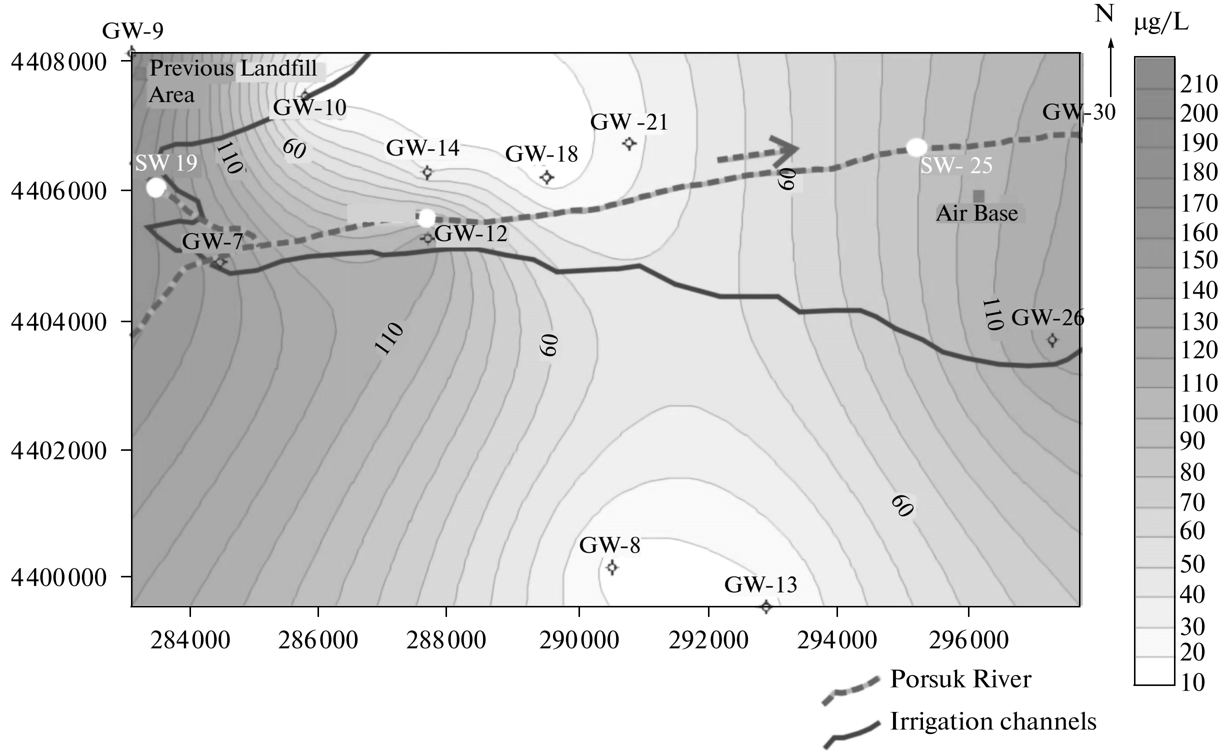

Fig. 10. Fe distribution map of the sampling locations in the dry period of 2008.

(229.50 μg/L) for the dry period of 2008 (Fig. 10). Both values are higher than allowable limit for drinking purpose.

The distributions of Mn for the wet and dry period of 2008 are shown in Figs. 11 and 12. The Mn concentration in SW-24 (85.06 and 56.15 μg/L), which is located close to GW-18 that has higher concentrations (466.80 and 413.00 μg/L) than allowable limit (50 μg/L). Thus, this can invoke a possible influence of surface water on the groundwater quality.

Finally, surface water influence can be mentioned for Ni content between SW-25 and GW-18 with concentrations of 23.56 and 22.67 μg/L, respectively (Fig. 13).

By the examination of the parallel changes in heavy metal and As concentrations in surface water and groundwater, pair of water samples was obtained (Table 4). The most prominent changes can be seen in As. Fe and Mn contents (Table 4). Variation in the

Table 4. Changes of parameters in the pairs of surface water-groundwater (parameters in bold exceed allowable limits in the water pairs)

Water Pairs		
Surface Water	Groundwater	Similarity in terms of parameters
sample no.	sample no.	dry and wet period
SW-15	GW-1	As, Cr
SW-19	GW-9	Fe, Pb, Cr, Cu, Ni, Zn, Al
SW-21	GW-12	As, Zn, Cr, Mn, Fe, Cu
SW-24	GW-8–GW-19–GW-21	Fe, As, Mn, Pb, Zn
SW-29	GW-31	As
SW-30	GW-32	As, Zn, Cr
SW-31	GW-33	As
SW-32	GW-34	As, Cr

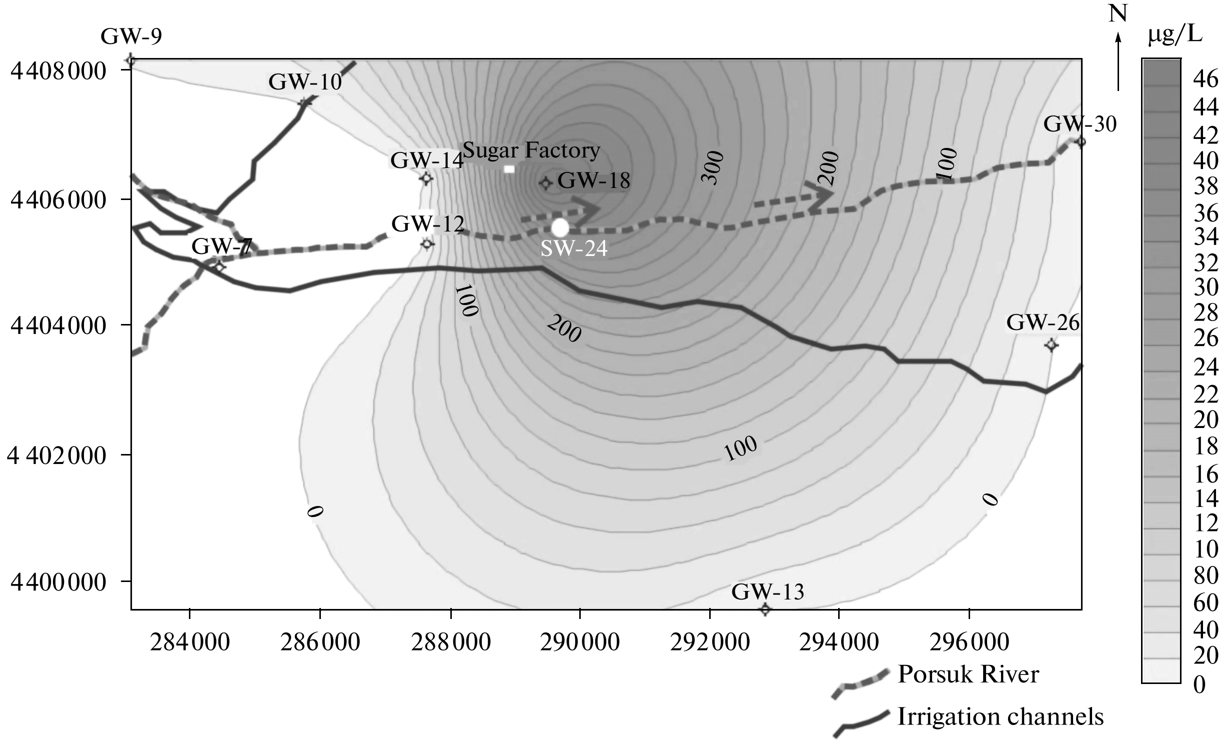

Fig. 11. Mn distribution map of the sampling locations in the dry period of 2008.

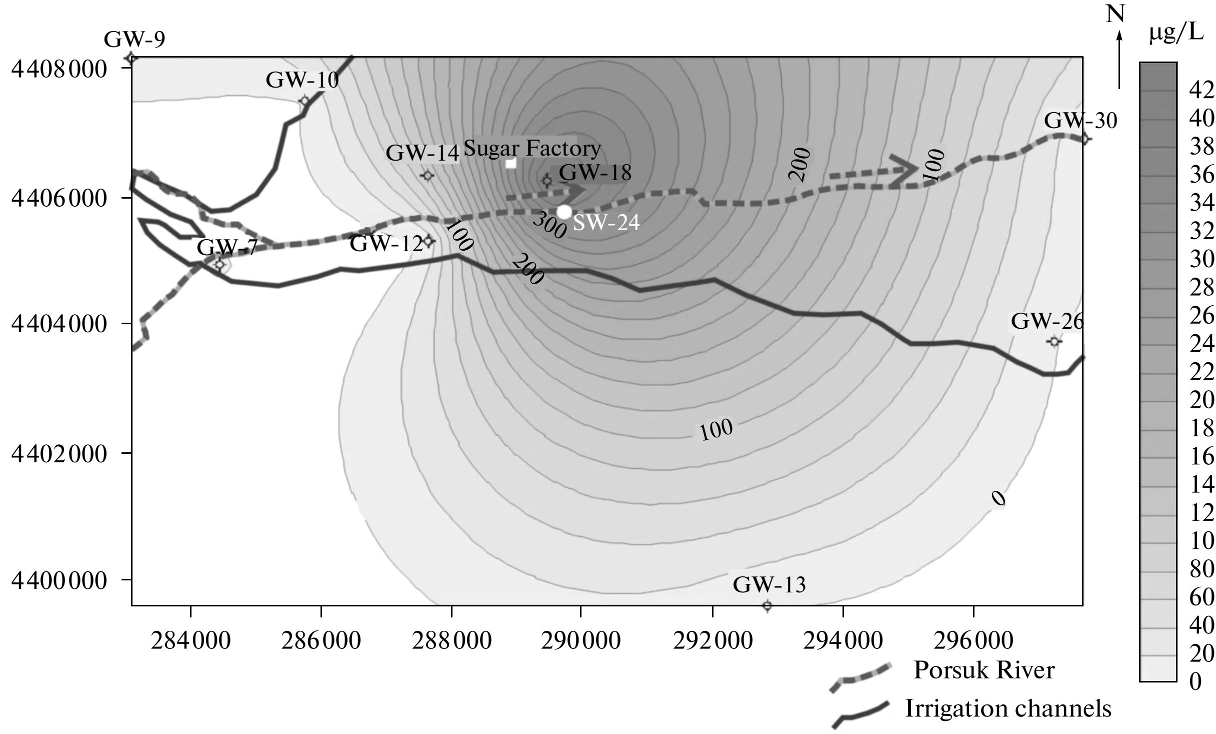

Fig. 12. Mn distribution map of the sampling locations in the dry period of 2008.

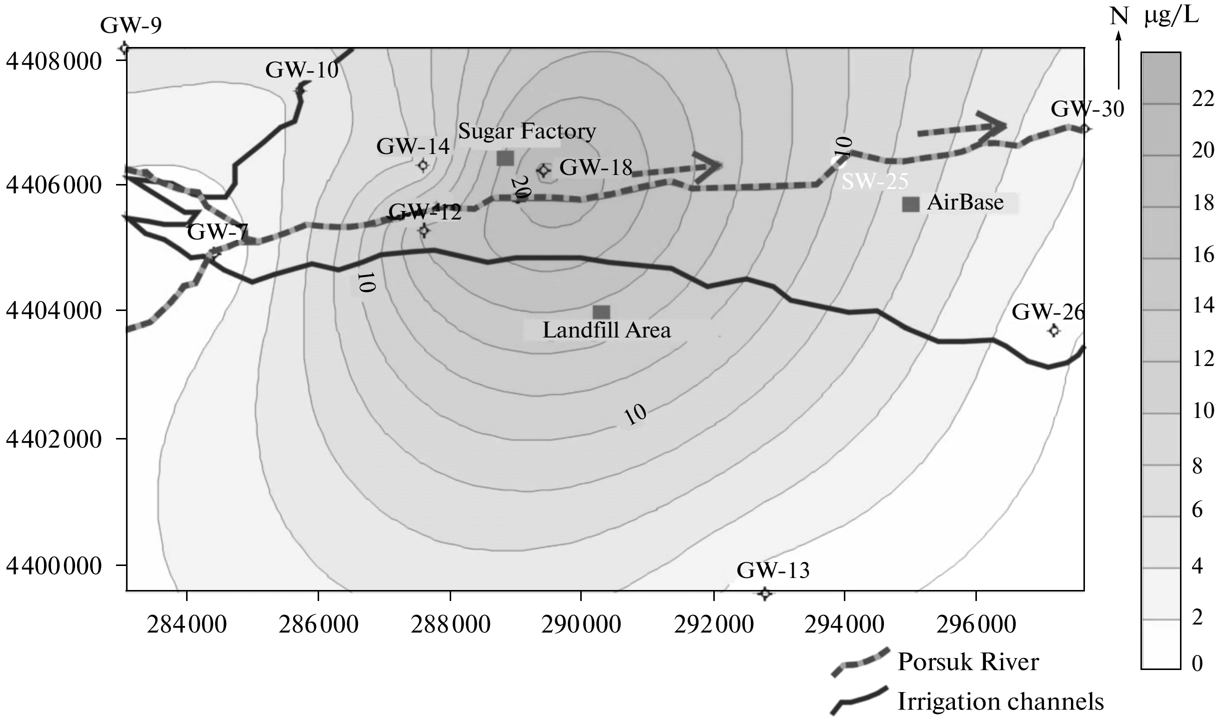

Fig. 13. Ni distribution map of the sampling locations in the dry period of 2008.

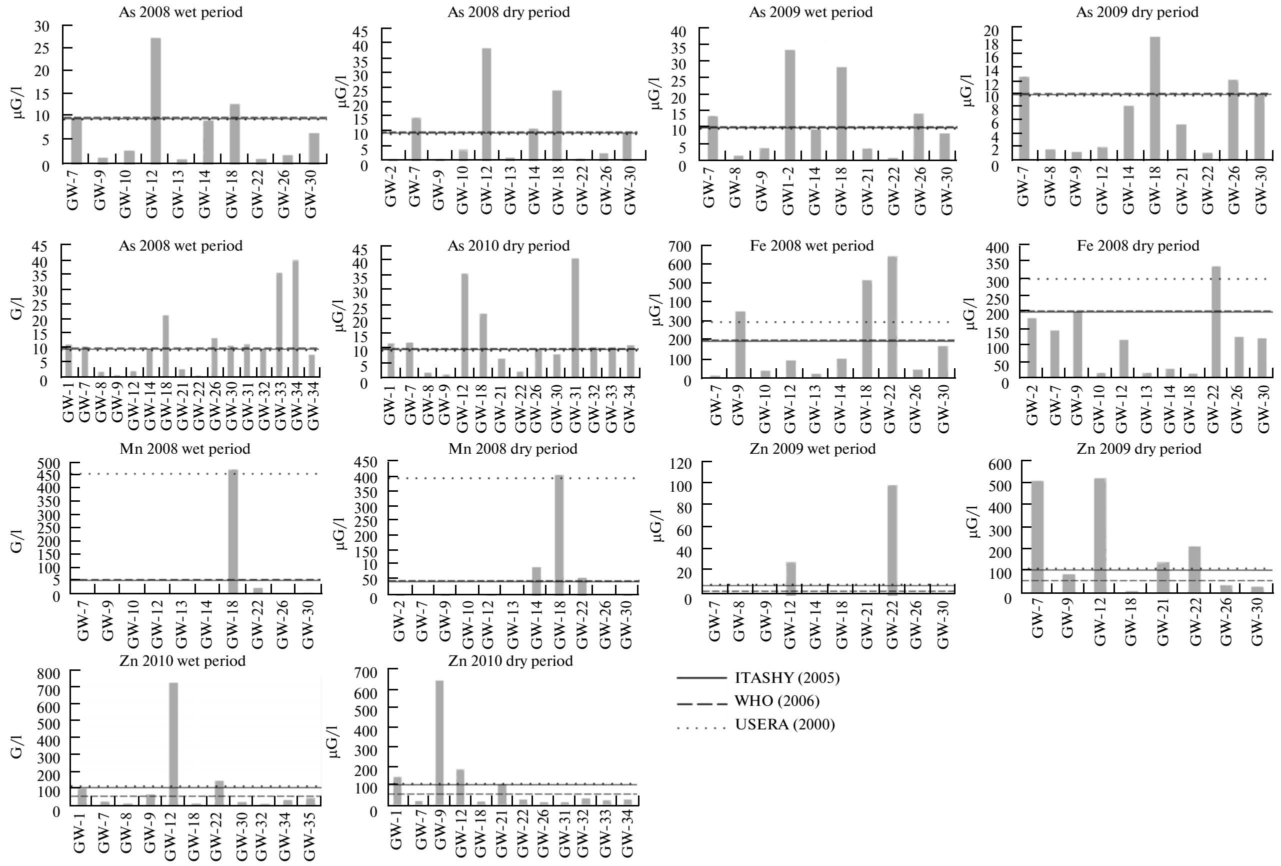

Fig. 14. Graphs of heavy metal contents of groundwater samples based on [4, 7, 9].

concentrations of As, Fe, Mn, and Zn in groundwater over time is given in Fig. 14 [4, 7, 9].

CONCLUSIONS

The groundwater in the study area is drawn from the alluvium and the Neogene limestone. Aquifer is open to contaminations. The industrial and agricultural contaminations in particularly lead to worsening of the groundwater, drinking and irrigation water quality. It is thought that the pollution is caused by the contamination of the groundwater through the agricultural and industrial activities directly, or by the discharge of the waste water from these activities to the Porsuk River without any treatment or with insufficient treatment. According to data on the heavy metal contents, the surface water is prone to contaminate groundwater due to recharge shallow groundwater along the some sections of the Porsuk River, especially after the treatment plant. Among the heavy metals that exceed the limit value, As is the most remarkable and has been observed in almost all water samples.

The ten groundwater-surface water pairs were determined in close proximity to each other. The temporal changes of these pairs show similarity in time. The similar changes in some heavy metal contents in the groundwater and surface water sample pairs which were collected in the same period of the time and have close locations to each other. Higher concentrations of heavy metals in the wells which are far from the river indicate a local contamination. The correlation coefficients of the heavy metals of the groundwater-surface water pairs in close proximity to each other that were collected to evaluate surface water-groundwater interactions were found higher at each year and at each period. The increase in concentrations of heavy metals in the samples taken especially in recent years and in the dry periods may be due to the increase in the activities during summer, in addition to the waters given from the Porsuk River to the irrigation channels.

The waste water of the sugar mill should not be discharged to the Porsuk River unless a sufficient treatment to prevent the contamination parameters in the groundwater and surface water samples are implemented.

High heavy metal concentrations were found especially in the areas of intensive agricultural and industrial activities.

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REFERENCES

1. Albek, E., Estimation of Point and diffuse contaminant loads to streams by non-parametric regression analysis of monitoring data, *Water, Air, and Soil Pollution*, 2003, vol. 147, pp. 229–243, doi:10.1023/A:1024592815576.
2. Gozler, Z., Cevher, F., Ergul, E., and Asutay, J., Geology of southern and middle part of Sakarya, *MTA Publications*, 1996, no. 9973, p. 97 [in Turkish].
3. Guney, Y., Porsuk River water and sediment's geotechnical, chemical and biological characteristic's seasonal variation and improving of the sediment wastes, *Anadolu Univ. Publications*, 2002, Eskisehir.
4. ITASHY, *Regulation on waters for human consumption 2005*, Official Gazette dated 17/02/2005, no. 25730 [in Turkish].
5. Olmez, E. and Yucel, B., Geothermal Energy Facilities of Eskisehir Region, *MTA Publications*, 1985, MTA Department of Energy Raw Materials Research and Exploration, pp. 1–18.
6. TDWS, *Turkish Drinking Water Standards*, Ankara: The Health Ministry, 2005.
7. USEPA, *The United States Environ. Protection Agency, Drinking Water Standards and Health Advisories*, Washington DC: Office of Water U.S. EPA, 2000.
8. WHO, *World Health Organization, Guidelines for Drinking-water Quality*, http://www.who.int/mediacentre/factsheets/fs372/en/, 2012.
9. WHO, *World Health Organization, Guidelines for Drinking-water Quality*, First Addendum to 3rd Edition, vol. 1, Recommendations, 2006.
10. Yuce, G., Pinarbasi, A., Ozcelik, S., and Ugurluoglu, D., Soil and water pollution derived from anthropogenic activities in the Porsuk River Basin, Turkey, *Environ. Geol.*, 2006, vol. 49, pp. 359–375, doi: 10.1007/s00254-005-0072-5.
11. Yuce, G., Spatial distribution of groundwater pollution in the Porsuk River Basin (PRB), Turkey, *In. J. Environ. Pol.*, 2007, vol. 30, pp. 539–547.