Spatial distribution of groundwater pollution in the Porsuk River Basin (PRB), Turkey

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Abstract: The groundwater in the alluvium aquifer of the Eskisehir Plain (EP) is polluted by wastewaters transported through Porsuk River, agricultural-industrial activities, river-groundwater interactions and unsanitary landfill. Porsuk River flows throughout the alluvium aquifer in the EP. In this study, the effects of anthropogenic activities on groundwater quality in the EP were investigated. Since the sewage system has been operated from 1998, the ammonia content of the groundwater has decreased, but the groundwater and Porsuk River water have high contents of nitrite, ammonium, phenol, phosphorus, AOX, sulphide, and heavy metals. Thus, groundwater in the EP is in a poor quality both for drinking and domestic purposes.

Keywords: river-groundwater interaction; groundwater contamination; nitrogen; phosphorus; phenol; AOX.

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Biographical notes: Galip Yuce (1961) graduated from Hacettepe University in 1984. He received his PhD in hydrogeology from Cukurova University, Turkey. He has worked for the General Directorate of Mineral Research and Exploration (MTA) and State Hydraulic Works (DSI) of Turkey. In 2000, he was appointed to Eskisehir Osmangazi University as a Senior Lecturer and Researcher. His main research interests are hydrogeochemistry, isotope hydrology, karst hydrogeology, and groundwater pollution. He has carried out several projects on hydrogeology and environmental subjects.

1 Introduction

Water is essential for survival. Misuse of water resources and poor water management cause degradation of water quality both in surface and groundwater systems. Water pollution, originating mostly from human activities in urbanised areas, has been observed all over the world, and a wide spectrum of contaminants such as nitrogen, phosphorus, chlorinated compounds, heavy metals, and pesticides have been reported. The PRB in Turkey has suffered from water pollution in respect of both surface water and groundwater resources. Especially, this pollution is very clear in Eskisehir district of the PRB, which has shallow aquifer conditions. Varieties of organic and inorganic wastes, some of which are harmful to human health, are directly discharged into the

Porsuk River. Nitrogen levels have become a concern owing to the increasing urbanisation of Eskisehir. The variation of this contamination with time is important because the Porsuk River is the only source for irrigation and domestic water in the Eskisehir metropolitan area. Overuse of nitrogen fertilisers, river-groundwater interaction, leaching from waste landfills, industrial and wastewater disposal systems, and land-use changes associated with urbanisation are the principal factors that increase pollution in the PRB.

A surface reservoir in the recharge area provides water for irrigation; wells where depths change from several metres to 133 m are also used for the same purpose. Fluctuations of the water table owing to seasonal variations and diverted surface water lead to strong interaction between the groundwater and soil water that is high in nitrates (Chen et al., 2005).

Organic contaminants in surface and groundwater of the PRB were assessed by collecting 22 water samples from the river and deep wells during two sampling campaigns conducted in 2001. In addition, previous analysis results compiled to compare with obtained recent results. First investigations were made by DSI (1975) and Özbek (1976). The General Directorate of State Hydraulic Works (DSI) investigated the effect of Porsuk River water on groundwater and on the region in cooperation with United Nation Development Project (UNDP) and WHO. Ölmez and Yücel (1985) investigated the thermal water potential of Eskisehir region; the thermal springs in Eskisehir city and their effect on groundwater contamination. Besides these investigations, the content of nitrogen compounds (NO_3, NO_2, and NH_3) in groundwater and Porsuk River water from agricultural activities was also investigated (Kacaroglu, 1991; Kacaroglu and Gunay, 1997a; 1997b). In 1988, 98% of public supply wells had been tested and their nitrate contents were more than 10 ppm above the allowable limits for drinking water according to the EPA (2003). Although the sewerage system was established in 1998, the contamination of nitrogen derivatives is still above the allowable limits for drinking water. Drinking water with nitrate concentrations above this limit can be toxic to young infants, leading to the blood disorder methemoglobinemia or blue baby syndrome. Nitrate in the groundwater is also sourced from wastewater of treatment plant effluent, agricultural activities and land use, and landfill leaching. Heavy metal pollution in water near unsanitary landfill area is also mentioned by Bakis (1996). Ozcelik (1998) investigated the variations in groundwater quality after the construction of the city sewerage system.

The unsanitary landfill contributes to pollution in the PRB. The leachate from this landfill is rich in heavy metals, organic substances, bacteria, and salts that may decompose readily by chemical and biochemical routes and infiltrate to surface water and to groundwater, causing one of the most important pollution factors.

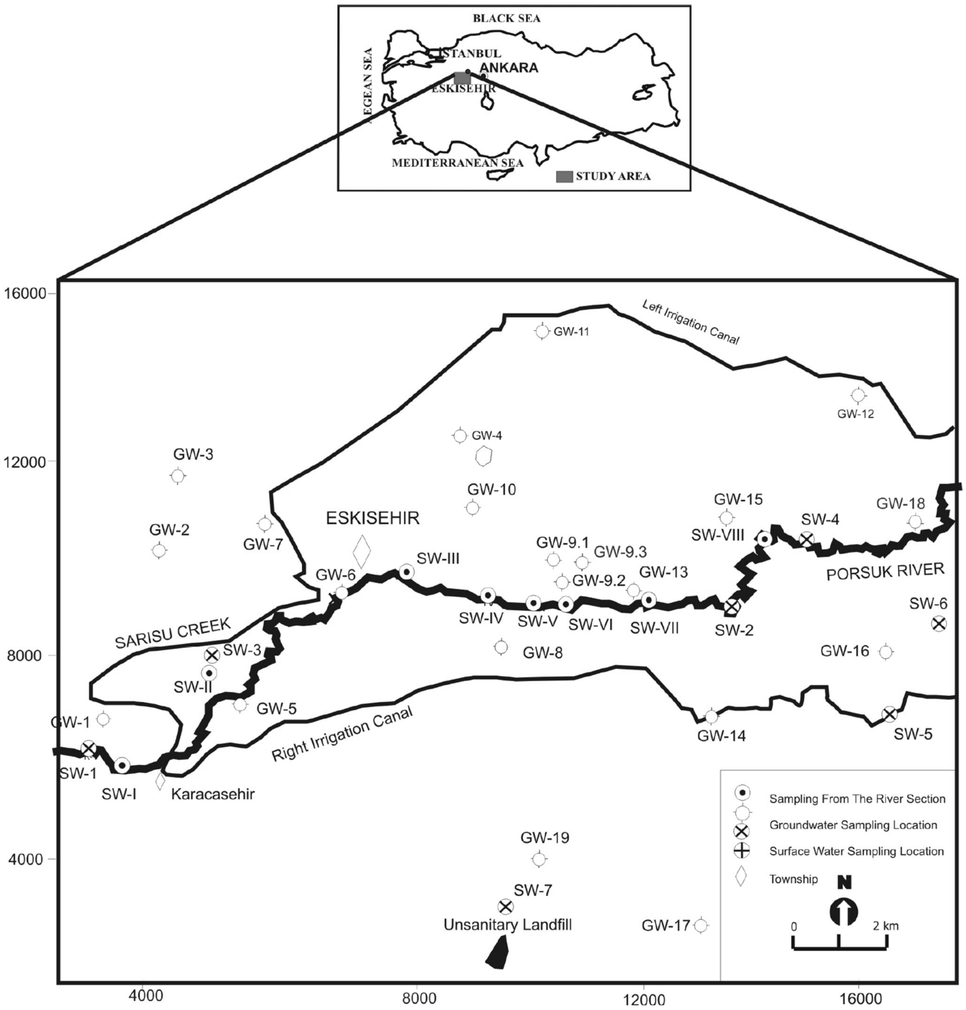
The objective of this study was to evaluate the influences of agricultural, industrial, and human activities on groundwater quality of the PRB after the sewerage system began operation in 1998.

2 Materials and methods

The study area is 500 km^2. The sampling locations were selected downstream of the contaminating points (Figure 1). A piezometric and hydrochemical study has been carried out in the PRB. Water for chemical analyses was sampled from the Porsuk River

(SW-1 … SW-6) and the deep wells (GW-1 … GW-19) (50–133 m depth) and a spring besides a treated river water (TW1). The surface water samples were taken directly from Porsuk River and irrigation channels and groundwater samples were collected either from springs or from deep wells. Values for the electrical conductivity (EC), temperature (°C), pH, hydraulic heads, and Eh were measured in situ. Error limits were ±0.5% for EC and ±0.1 for pH.

Figure 1 Location map



The parameters of TDWS are taken into consideration during the groundwater pollution surveys of the surface and groundwater in wet and dry periods. The samples were collected based on Turkish Water Sampling Standards and Analysing Methods (Turkish State Newspaper, 2004).

The samplings were performed in May and October 2001. In sampling, double-capped hard plastic bottles were used for water analyses. The anion and cation samples were filtered (0.45 μm) and stored at a constant temperature of 4°C. The cation and heavy metal samples were acidified to pH < 2 by nitric acid. Because sulphur and nitrite could not be analysed in the field, they were protected by adding four drops of 2N zinc acetate solution per 100 ml of sample and 40 mg $HgCl_2$ per 1 litre of sample for sulphur and nitrite, respectively. For phenol, COD (chemical oxygen demand), ammonium-N, oil and grease analyses, H_2SO_4 solution was added until the pH was ≤2, at +4°C. For free chloride, BOD (biological oxygen demand), phosphorus, TDS (total dissolved solids), SSM (suspended solid material), ammonia and nitrate analyses, the samples were protected at +4°C and were analysed within 1–2 hours. The analyses were performed in the laboratory of Anadolu University Eskisehir with ICP-MS and ion chromatography.

3 Geological and hydrogeological background

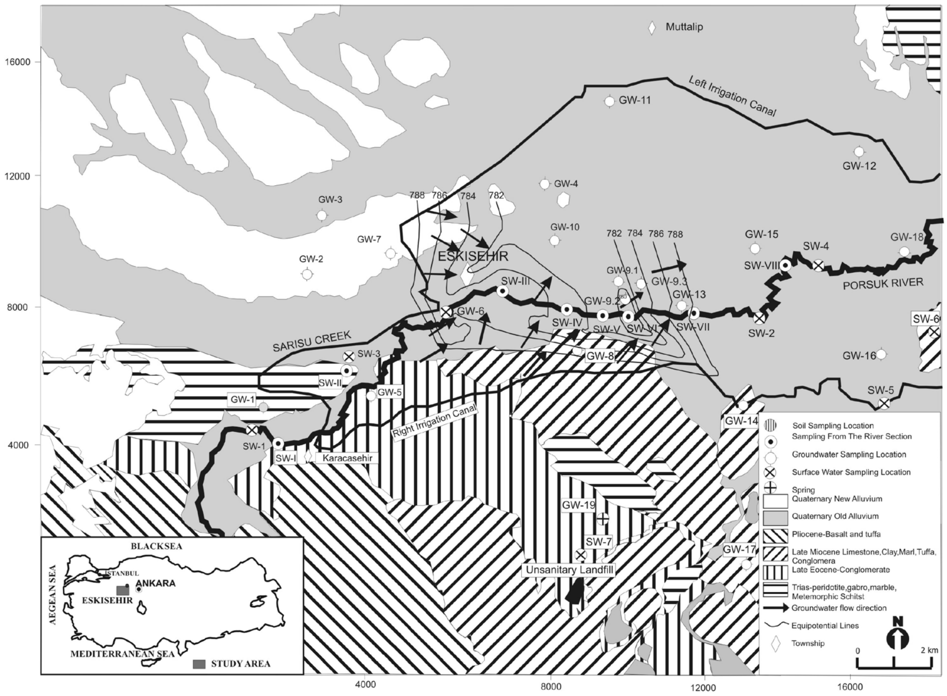
The geological framework of the PRB is shown in Figure 2. The city of Eskisehir is located in a plain, which is bounded by high mountains both in the north and in south. The Porsuk River flows on this plain from west to east (Figure 2). The basement rocks in the region are schist, crystalline limestone, and ophiolitic mélange in Triassic age (Gozler et al., 1996) and contact between them is tectonic. Basement rocks are unconformably overlain by conglomerates, marls, claystone, limestone, clays, and tuffs of Eocene. Miocene and Pliocene age tuffs, agglomerates, basalts and clastic rocks unconformably overlie Eocene and much older units. Quaternary deposits can be classified as old and young alluvium. The old alluvium of Pleistocene (Villafrancian) outcrops at the edges of Eskisehir plain, and the total thickness reaches 120 m. About 15 m thick young alluvial deposits, mainly carried by the Porsuk River, are deposited in the Eskisehir plain.

The crystalline limestone, and ophiolitic mélange, conglomerate and sandstone levels of Eocene yield limited amounts of groundwater. The main aquifers are old and young alluviums and limestone levels of Neogene. The young alluvium accumulated along the Porsuk River contributes to the leakage of nitrate into the aquifer system.

The groundwater level is high in Eskisehir region, downgradient of the PRB, varies between 1–6 m from the surface. The water table contour map (hydraulic head distribution) was prepared by evaluating the water levels of deep wells. The groundwater is discharged to the river, according to the flow line map at the left bank of Porsuk River. Although this trend is observed in higher altitudes, this situation disappears owing to the intensive pumping by the drilled wells at the riverbank. At the right bank, groundwater recharges to the river (Figure 2).

On the other hand, the unsanitary landfill is located in Takahasan valley, formed of carbonate rocks, which has semi-permeable layers. The groundwater flow, in vicinity of the unsanitary landfill area, discharges into the main aquifer system that extends towards south.

Figure 2 Geological map



Source: After Yuce et al. (2006)

4 Results and discussion

The previous analyses results of the water samples collected from the deep wells (depth varies from 50 to 133) are given in Tables 1(a)–(c). Comparison of the obtained results from Porsuk River by 2001 (Table 2(a)) with the previous results (Tables 2(b) and 2(c)), shows that water quality is decreasing. However, NO_3 contents decreased in some region, but some of those are still in high level.

Table 1(a) Analysis results of groundwater samples

Sample no.	*Sampling date*	*Results* (mg/l)				
		Boron	*Nitrite*	*Nitrate*	*SSM*	*Ammonia*
GW-3	17.04.1998	0.03	0.01	24.81	0.00	0.01
GW-6	20.04.1998	0.00	0.03	26.27	5.00	0.00
GW-7	20.04.1998	0.00	0.01	109.6	1.00	0.00
GW-8	17.04.1998	0.48	0.26	77.97	0.00	0.43
GW-9	20.04.1998	0.00	3.62	16.83	3.00	0.06
GW-10	17.04.1998	0.06	0.02	57.59	0.00	0.05
GW-11	17.04.1998	0.03	0.03	17.06	0.00	0.01
GW-13	17.04.1998	0.19	9.21	60.25	0.00	0.18
GW-15	20.04.1998	0.00	0.01	12.09	2.00	0.04

Source: Ozcelik (1998)

Table 1(b) Analysis results of groundwater samples according to the TDWS, 1997

Sample no.	*Well depth* (m)	*Sampling date*	*Boron* (mg/l) *Results*	*Boron* *RL* 1 / *MCL* 2	*Free chloride* (mg/l) *Results*	*Free chloride* *RL* 0.1 / *MCL* 0.5	*Nitrite* (mg/l) *Results*	*Nitrite* *RL* 0 / *MCL* 1	*Nitrate* (mg/l) *Results*	*Nitrate* *RL* 25 / *MCL* 50	*Phenol* (mg/l) *Results*	*Phenol* *RL* 0 / *MCL* 5.10^{-4}	*SSM* (mg/l) *Results*	*SSM* *RL* 0 / *MCL* 1	*Ammonia* (mg/l) *Results*	*Ammonia* *RL* 0 / *MCL* 0.05	*AOX* (mg/l) *Results*	*AOX* *RL* 0 / *MCL* 0.01
GW-1	50	22.05.2001	2.10	OMCL	0.03	RL	0	RL	39.0	ORL	–	–	3.5	OMCL	4.65	OMCL	–	–
		18.10.2001	0.55	RL	0.02	RL	3	OMCL	26.0	ORL	–	–	4.0	OMCL	7.95	OMCL	–	–
GW-3	50	22.05.2001	0.70	RL	0.08	RL	4	OMCL	19.0	RL	–	–	5.0	OMCL	3.54	OMCL	–	–
		19.10.2001	–	–	0.02	RL	4	OMCL	20.0	RL	0.12	OMCL	9.0	OMCL	2.20	OMCL	–	–
GW-5	105	24.05.2001	0.75	RL	0.03	RL	6	OMCL	22.0	RL	0.01	OMCL	4.0	OMCL	3.47	OMCL	–	–
		18.10.2001	–	–	0.01	RL	3	OMCL	15.0	RL	0.00	RL	5.0	OMCL	2.90	OMCL	–	–
GW-6	90	23.05.2001	0.90	RL	0.04	RL	1	MCL	23.3	RL	–	–	5.0	OMCL	2.74	OMCL	–	–
		18.10.2001	–	–	–	–	–	–	–	–	–	–	–	OMCL	8.06	OMCL	–	–
GW-7	–	23.05.2001	0.95	RL	0.05	RL	10	OMCL	56.0	OMCL	–	–	1.5	OMCL	3.40	OMCL	–	–
		19.10.2001	0.39	RL	0.00	RL	4	OMCL	59.0	OMCL	–	–	9.0	OMCL	2.45	OMCL	–	–
GW-8	133	23.05.2001	0.95	RL	0.05	RL	0	RL	44.0	ORL	–	–	4.5	OMCL	4.70	OMCL	–	–
		19.10.2001	0.45	RL	0.04	RL	3	OMCL	37.0	ORL	0.16	OMCL	5.0	OMCL	3.61	OMCL	–	–
GW-9.2	–	25.05.2001	1.35	ORL	0.07	RL	6	OMCL	18.0	RL	0.06	OMCL	3.0	OMCL	4.19	OMCL	–	–
		19.10.2001	0.65	RL	0.00	RL	4	OMCL	15.0	RL	0.08	OMCL	10.0	OMCL	2.18	OMCL	–	–
GW-10	–	25.05.2001	0.50	RL	0.05	RL	0	RL	38.0	ORL	–	–	2.0	OMCL	3.32	OMCL	–	–
GW-11	–	25.05.2001	0.40	RL	0.06	RL	1	RL	17.0	RL	–	–	1.5	OMCL	2.83	OMCL	–	–
GW-12	50	25.05.2001	0.60	RL	0.05	RL	2	OMCL	5.3	RL	–	–	2.0	OMCL	3.53	OMCL	–	–
GW-13	100	30.05.2001	0.75	RL	0.01	RL	3	OMCL	20.0	RL	–	–	2.0	OMCL	4.25	OMCL	–	–
		19.10.2001	–	–	0.01	RL	3	OMCL	22.0	RL	7.70	OMCL	3.0	OMCL	6.73	OMCL	–	–
GW-15	–	25.05.2001	0.90	RL	0.07	RL	0	RL	15.8	RL	–	–	10.5	OMCL	4.36	OMCL	–	–
GW-16	64	25.05.2001	1.20	ORL	0.01	RL	3	OMCL	11.0	RL	–	–	1.5	OMCL	2.27	OMCL	–	–
		19.10.2001	0.65	RL	0.02	RL	3	OMCL	21.0	RL	–	–	3.0	OMCL	<0.02	ORL	–	–
GW-18	–	25.05.2001	0.55	RL	0.01	RL	4	OMCL	20.2	RL	–	–	4.5	OMCL	3.31	OMCL	–	–
GW-19	–	25.05.2001	0.55	RL	0.02	RL	2	OMCL	42.0	ORL	–	–	1.5	OMCL	2.02	OMCL	–	–
		19.10.2001	–	–	0.00	RL	3	OMCL	42.0	ORL	6.70	OMCL	2.0	OMCL	1.01	OMCL	–	–
TW-1	–	19.10.2001	–	–	0.70	MCL	4	OMCL	9.0	RL	6.60	OMCL	2.0	OMCL	2.76	OMCL	0.25	OMCL

RL: Recommended Level.
ORL: Over RL.
MCL: Maximum Contamination Level.
OMCL: Over MCL.
GW: groundwater.
TW: tap water.

Source: After Yuce et al. (2006)

Table 1(c) Analysis results of groundwater samples according to the TIWS, 1997

		Boron (mg/l)		*Free Chloride* (mg/l)		*Nitrite* (mg/l)		*Nitrate* (mg/l)		*Phenol* (mg/l)		*SSM* (mg/l)		*Ammonia* (mg/l)		*Ammonium* (mg/l)		*Oil-Gress*		*Sulfide*		*COD*		*TDS*		*P*		*BOD*	
Sample No	*Sampling Date*	*Results*	*Class **	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**	*Results*	*Class**
GW-1	22.05.2001	2.10	IV	0.03	III	0	I	39.0	II	–	–	3.5	I	4.65	–	4.91	IV	–	–	0.08	IV	25	I	475	I	0.026	II	11	III
	18.10.2001	0.55	II	0.02	II	3	IV	26.0	II	–	–	4.0	–	7.95	–	7.85	IV	–	–	0.02	IV	–	–	–	–	–	–	–	–
GW-3	22.05.2001	0.70	II	0.08	IV	4	IV	19.0	I	–	–	5.0	I	3.54	–	3.73	IV	–	–	0.05	IV	16	I	466	I	0.031	II	7	II
	19.10.2001	–	–	0.02	II	4	IV	20.0	I	0.12	–	9.0	–	2.20	–	2.35	III	–	–	0.04	IV	–	–	–	–	–	–	–	–
GW-5	24.05.2001	0.75	II	0.03	III	6	IV	22.0	I	0.01	–	4.0	I	3.47	–	3.65	IV	23.6	IV	0.06	IV	17	I	375	I	0.034	II	6	II
	18.10.2001	–	–	0.01	I	3	IV	15.0	I	0.00	–	5.0	–	2.90	–	2.85	IV	36.2	IV	0.02	IV	–	–	–	–	–	–	–	–
GW-6	23.05.2001	0.90	II	0.04	II	1	IV	23.3	II	–	–	5.0	I	2.74	–	2.79	III	–	–	0.06	IV	4	I	597	II	0.03	II	2	I
	18.10.2001	–	–	–	–	–	IV	–	–	–	–	–	–	8.06	–	7.98	–	–	–	–	–	–	–	–	–	–	–	–	–
GW-7	23.05.2001	0.95	II	0.05	II	10	IV	56.0	III	–	–	1.5	I	3.40	–	3.57	IV	–	–	0.06	IV	21	I	430	I	0.036	II	9	III
	19.10.2001	0.39	I	0.00	I	4	IV	59.0	III	–	–	9.0	–	2.45	–	2.46	III	–	–	0.03	IV	–	–	–	–	–	–	–	–
GW-8	23.05.2001	0.95	II	0.05	II	0	I	44.0	II	–	–	4.5	I	4.70	–	4.12	IV	–	–	0.07	IV	22	I	613	II	0.008	I	8	II
	19.10.2001	0.45	I	0.04	I	3	IV	37.0	II	0.16	–	5.0	–	3.61	–	3.53	IV	–	–	0.04	IV	–	–	–	–	–	–	–	–
GW-9.1	25.05.2001	1.35	III	0.07	III	6	IV	18.0	I	0.06	–	3.0	I	4.19	–	4.14	IV	2.8	IV	0.04	IV	9	I	541	II	0.019	I	8	II
	19.10.2001	0.65	II	0.00	II	4	IV	15.0	I	0.08	–	10.0	–	2.18	–	2.11	III	–	–	0.03	IV	–	–	–	–	–	–	–	–
GW-10	23.05.2001	0.5	I	0.05	I	0	I	38	II	–	–	2	I	3.32	–	3.48	IV	–	–	0.07	IV	23	I	376	I	0.004	I	13	III
GW-11	23.05.2001	0.4	I	0.06	I	1	IV	17	I	–	–	1.5	I	2.83	–	2.97	III	–	–	0.08	IV	45	I	223	I	0.013	I	20	III
GW-12	23.05.2001	0.6	II	0.05	II	2	IV	5.3	I	–	–	2	I	3.53	–	3.43	IV	–	–	0.04	IV	–	–	–	–	–	–	–	–
GW-13	30.05.2001	0.75	II	0.01	II	3	IV	20.0	I	–	–	2.0	I	4.25	–	4.31	IV	–	–	0.03	IV	13	I	294	I	0.02	I	16	III
	19.10.2001	–	–	0.01	–	3	IV	22.0	I	7.70	–	3.0	–	6.73	–	7.12	IV	–	–	0.03	IV	–	–	–	–	–	–	–	–
GW-15	25.05.2001	0.9	II	0.07	II	0	I	15.8	I	–	–	10.5	I	4.36	–	4.4	IV	–	–	0.05	IV	8	I	575	II	0.018	I	8	II
GW-16	25.05.2001	1.20	III	0.01	III	3	IV	11.0	I	–	–	1.5	I	2.27	–	2.11	III	–	–	0.03	IV	9	I	551	II	0.025	II	7	II
	19.10.2001	0.65	II	0.02	II	3	IV	21.0	I	–	–	3.0	–	<0.02	–	<0.02	I	–	–	0	I	–	I	477	I	0.007	I	3	I
GW-17	25.05.2001	0.85	II	0.19	IV	0	I	11.0	I	–	–	20.5	I	–	–	1.84	III	16.4	IV	0.03	IV	31	II	279	I	0.17	III	14	III
GW-18	25.05.2001	0.55	II	0.01	II	4	IV	20.2	I	–	–	4.5	I	3.31	–	3.34	IV	–	–	0.04	IV	4	I	385	I	0.027	II	3	11.0
GW-19	25.05.2001	0.55	II	0.02	II	2	IV	42.0	II	–	–	1.5	I	2.02	–	2.00	III	–	–	0.03	IV	9	I	343	I	0.012	I	3	I
	19.10.2001	–	–	0.00	–	3	IV	42.0	II	6.70	–	2.0	–	1.01	–	1.07	I	–	–	0	I	–	–	–	–	–	–	–	–
TW-1	19.10.2001	–	–	0.70	–	4	–	9.0	–	6.60	–	2.0	–	2.76	–	3.75	–	–	–	–	–	–	–	–	–	–	–	–	–

I: Very good; II: Good; III: Bad; IV: Very bad.
*The class is based on Turkish Irrigation Water Standard.

Source: After Yuce et al. (2006)

Table 2(a) Analysis results of Porsuk River Water at the different sampling points (by 2001)

Water quality parameters	*Sampling points*				
	SW-1	*SW-2*	*SW-4*	*SW-5*	*SW-6*
Boron (mg/L)	–	5.5	5.5	0.85	1.4
Free chloride	–	0.09	0.1	0.19	0.05
Nitrite (mg/L)	0.17	2	–	0	0
Nitrate (mg/L)	3.68	4.4	–	11	5.3
SSM (mg/L)	20	16	–	20.5	11
NH_4 (mg/L)	–	2.48	13.28	2.36	2.94
Oil and grease	–	–	3.6	16.4	–
Sulphide	–	0.04	0.08	0.03	0.04
COD	–	44	92	31	27
TDS	363	302	397	279	280
Total P	–	0.08	0.68	0.17	0.18
BOD	–	22	46	14	23

Table 2(b) Analysis results of Porsuk River Water at the different sampling points (by 1999)

Water quality parameters	*Sampling points*							
	SW-I	*SW-II*	*SW-III*	*SW-IV*	*SW-V*	*SW-VI*	*SW-VII*	*SW-VIII*
Temperature (°C)	2.4	23	24	24	23	24	22.5	22.5
pH	6.8	7.2	7.5	7.8	6.1	7.5	7.6	7.7
DO (mg/L)	7.95	6.58	7.24	6.88	6.82	6.63	6.98	2.42
Oxygen Saturation (%)	97.7	84.5	90.7	87.3	86.7	85.6	89	30.7
Chloride (mg)	10.5	10.1	10.8	10.5	15.6	13.4	13	3.5
Sulphate (mg/L)	63	32	52	44	54	49	56	71
NH_4 (mg)	1.90	12.36	1.70	1.36	1.81	1.88	1.74	16.41
Nitrit (mg/L)	0.49	0.10	0.26	0.26	0.86	0.99	1.32	1.65
Nitrate (mg/L)	4.43	2.22	5.32	6.65	7.97	8.42	9.30	9.75
Total P (mg/L)	0.12	0.08	0.09	0.08	0.11	0.11	0.13	1.13
TDS (mg/L)	334	302	324	274	340	350	342	430
COD (mg/L)	12	16	16	12	20	20	24	76
BOD (mg/L)	4.95	1.65	1.65	0	3.56	8.25	6.6	79.6
Oil and grease (mg/L)	8	8.4	5.6	6	1.6	1.2	13.2	6.4
Fenolic material (SW-Volatile) (mg/L)	0	0.12	0	0.06	0	0	0	0.18
F (mg/L)	0.5	0.28	0.33	0.33	0.32	0.32	0.3	0.41
Free chloride (mg/L)	0.05	0.03	0.07	0	0.08	0.06	0	0
Sulphide (mg/L)	0.14	0.17	0.12	0.14	0.12	0.09	0.21	0.09
Boron (mg/L)	0.158	0.129	0.198	0.168	0.2	0.215	0.238	0.359
Al (mg/L)	0.03	0.06	0.22	0.11	0.21	0.31	0.1	0.18

Source: EGDE (1999)

Table 2(c) Analysis results of Porsuk River Water at the different sampling points (by 2000)

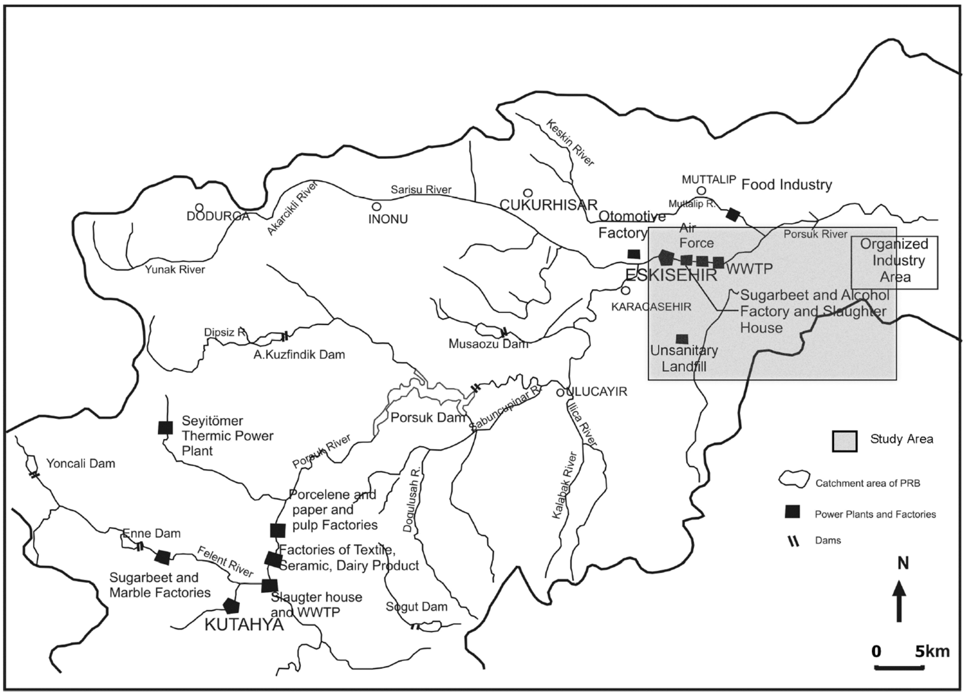
Water quality parameters	*Sampling points*							
	SW-I	*SW-II*	*SW-III*	*SW-IV*	*SW-V*	*SW-VI*	*SW-VII*	*SW-VIII*
Temperature (°C)	2.5	1.2	3	4.2	4.5	6.1	6.1	9.4
pH	8.49	8.5	7.7	8	7.9	7.3	7	8
Chloride (mg)	8.14	17.1	5.39	12.2	17.9	53.4	24.8	52.6
Sulphate (mg/L)	<40	<40	40850	<40	<40	<40	73.1	47.3
NH_4 (mg)	0.08	0.06	0.05	0.05	0.51	1.02	0.33	3.25
Nitrite (mg/L)	0.33	0.24	0.25	0.24	0.43	1.39	0.68	2.16
Nitrate (mg/L)	13.38	17.10	23.30	17.63	22.33	42.17	31.50	13.38
Total P (mg/L)	0.1	0.06	1.86	0.22	0.3	0.74	0.56	3.26
COD (mg/L)	78.6	39.9	76.2	77.4	34.5	816	274.5	700.8
BOD (mg/L)	41.8	21	42.8	41.4	<4	441	147	438
TOC (mg/L)	168.6	157.8	174.3	165.3	164.7	190.5	176.1	159
Cd	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

SW-I: Enterance to Plain
SW-II: Close to The Textile Factory
SW-III: Under the bridge
SW-IV: Middle Point
SW-V: Before Sugar Beet Factory
SW-VI: After Sugar Beet Factory
SW-VII: After the slaughterhouse
SW-VIII: Exit of the City.

Source: EGDE (2000)

The principal contamination sources are given in Figure 3 in the catchment area of the Porsuk River, namely Seyitomer Thermal Electric Power Plant (STEPP), abattoir of Kutahya city, Nitrogen, and Sugar-beet factory. Especially, STEPP is used a variety of chemicals in its cooling water, including chlorine as disinfectant to prevent biofouling, and metal-complexing agents to prevent scale build up. The polluted water reaching the Porsuk dam has the same high contents of NO_3-N, BOD, and DO and except for NO_2 and total P. The existence of high nitrogen and phosphorus at the outlet of Porsuk dam is owing to the organic substances in the sediments of the hypolimnion zone of the dam reservoir putting away the phosphorus from the reservoir water (Drever, 1997). Ferric oxides absorb phosphorus and when oxides are reduced; large amounts of phosphates are transferred into the water. Under anaerobic dam-lake conditions, bacteria in the surface sediments also contribute to important amounts of phosphate. The increases in values are observed except for nitrogen and phosphorus from outlet of Porsuk dam until Eskisehir city center.

Figure 3 Plants which discharge their waste water to Porsuk River in Kutahya and Eskisehir Region. Marble plant, sugar beet plant, slaughterhouse, thermic power plant, textile plant, food industry etc

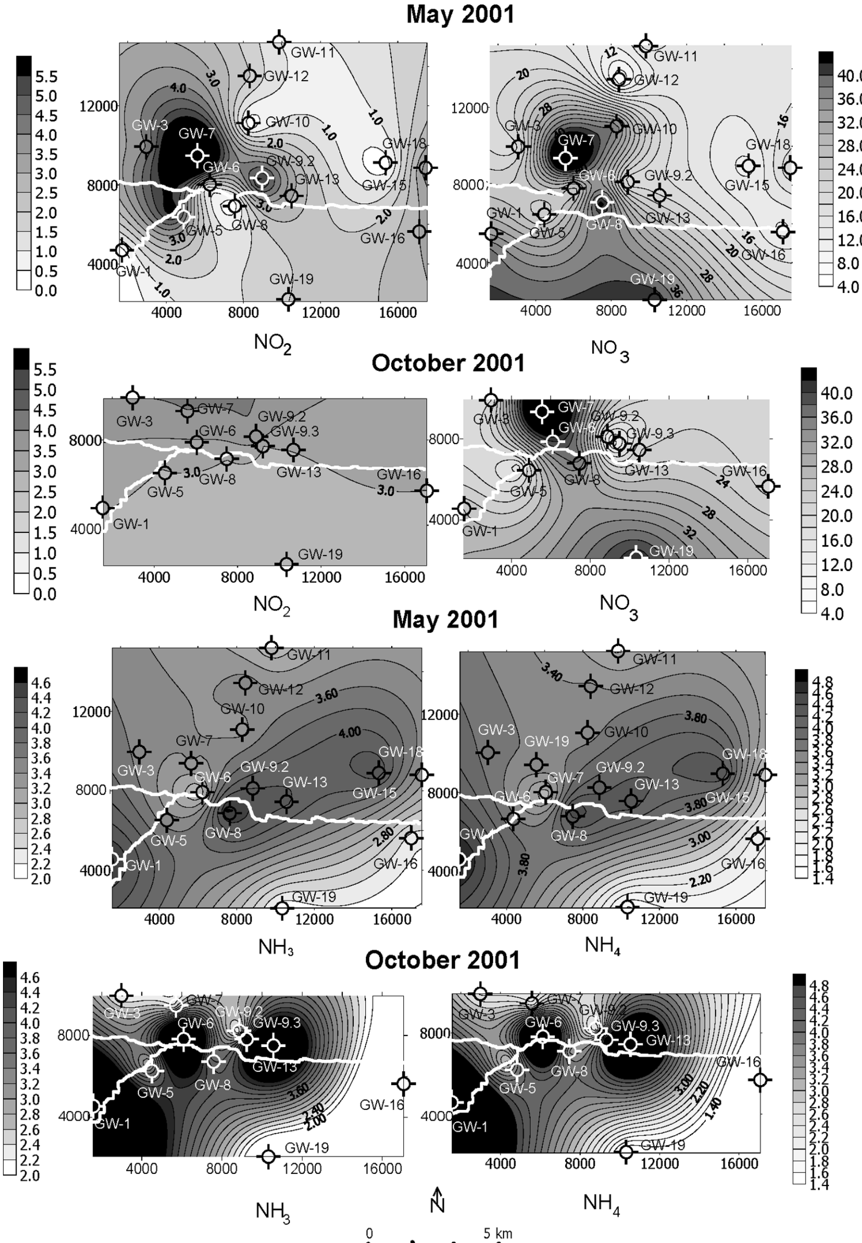


Source: After Su-Yapi (2001)

As Tables 1(b) and 1(c) show, ammonia and ammonium are high in all samples, and nitrite and nitrate partly exceed the allowable limits. Oil and grease values and sulphide are also high in some water samples. The water samples GW-3, GW-5, GW-8, GW-9.2, GW-13, GW-19, and TW-1 have very high phenol content than the maximum limit of 0.0005 mg/l for drinking water. This high phenol is possibly sourced from chlorine pesticides and industrial wastes (Domenico and Schwartz, 1990) that may mainly sourced the wastewater of STEPP. The phenol content of tap water (TW-1) after the Water Treatment Plant is in high values that sourced from the chlorinated process. (Tables 1(b) and 1(c)). Phenol is an extremely toxic material; it is widely used in agriculture and pesticides (Ren, 2002), and is used to make dyes, pesticides, lubricating oils and solvents. It also naturally occurs in pinewood and pine needles, and coal tar (www.nsc.org/library/chemical/Phenol.htm; www.atsdr.cdr.gov/tfacts115.html).

The highest values of NO_2, NO_3, NH_3, and NH_4 were observed in the central and eastern parts of the Eskisehir Region. The spatial distribution of the seasonal variations of nitrogen derivatives in groundwater is given in Figure 4. The maximum NO_2, NO_3, NH_3, and NH_4 values match into intensive populated area and municipal waste deposit, sugar factory, and wagon and locomotive construction factory. Furthermore, the application of nitrogen containing fertilisers such as $(NH_4)_2SO_4$ in irrigation forms aerial source for nitrate contamination. The NH_3, NO_2, NO_3 values of Porsuk River have increased compared to those of previous years (SW-2 and SW-4) (Figure 5(a) and 5(b)). Oil and grease contents are high in SW-4, SW-5, GW-6, GW-9.2, GW-13, and TW-1. Boron has increased. Especially samples of SW-4, GW-10, and GW-11 are getting worse with the waste load from the sugar factory and the Organised Industrial Area. At SW-4, phenolic material, free chlorine, and sulphur values have increased and a reductive environment is formed.

Figure 4 Spatial distribution of NO_2, NO_3, NH_3, NH_4 contents in groundwater samples



Source: After Yuce et al. (2006)

Figure 5(a) Variations of chemical parameters in time of the samples taken from Porsuk River (SW-I … SW-VIII)

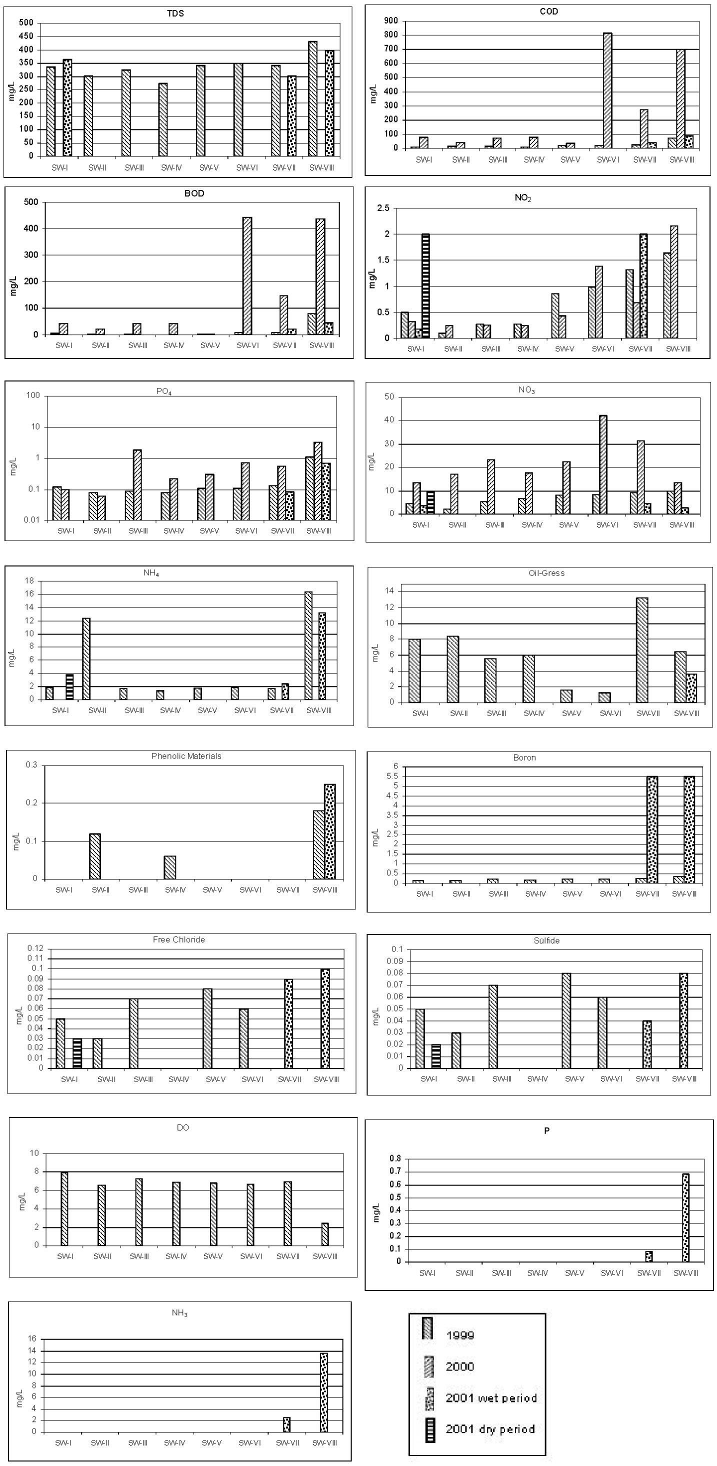
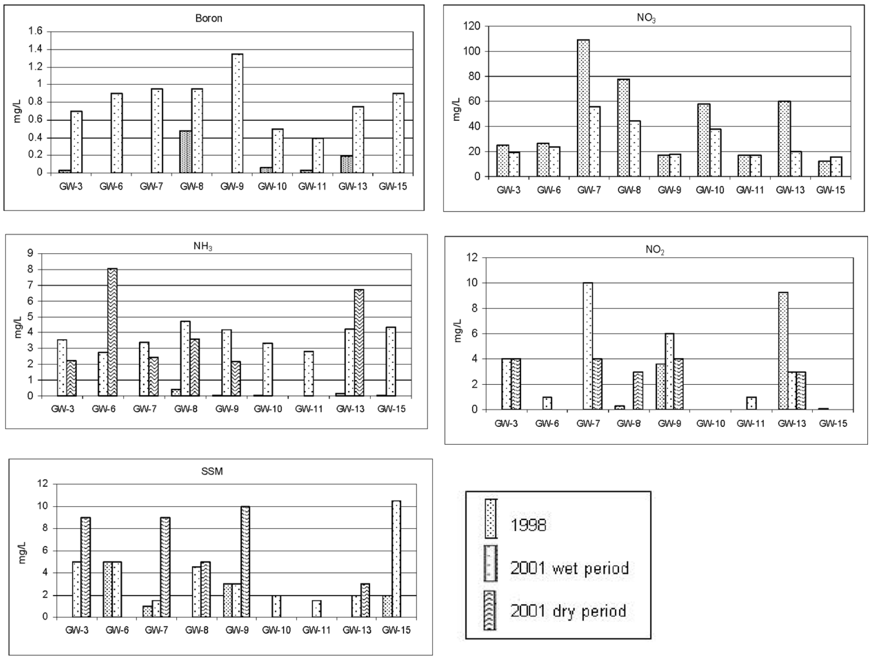


Figure 5(b) Variations of chemical parameters in time of the samples taken from groundwater (GW-1 … GW-19)

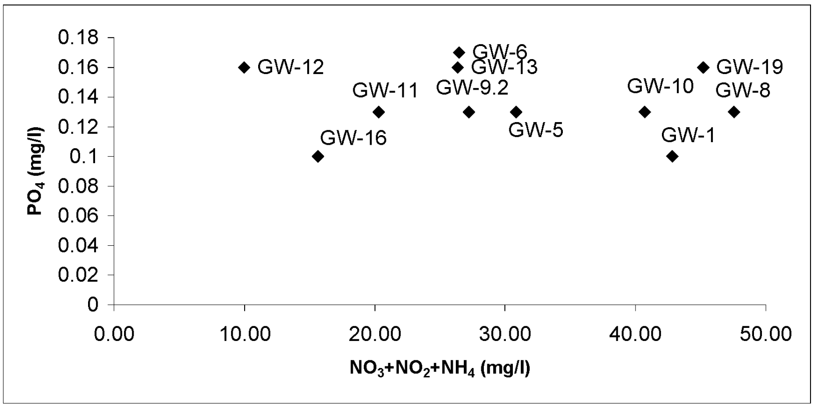


Besides the nitrogen compounds, another other pollutant is phosphorus. Dissolved phosphorus is found as phosphoric acid (H_3PO_4) in waters and it decomposes to orthophosphate (H_2PO_4). Dissolved phosphorus is quickly absorbed by soil and has a low mobility in groundwater (Fetter, 1999). Samples GW-1, GW-3, GW-5, GW-6, GW-7, GW-15, and GW-18 have high phosphorous contents. The origin of this surplus phosphorus in groundwater is seepage from the sewage system (Vanloon and Duffy, 2000). Mixing sewage water (high organic load) with chlorinated supply water may lead to further pollution by toxic chlorinated and recalcitrant compounds. Moreover, changes in groundwater chemistry may also change the chemical conditions under which the pollutants were immobilised, thus mobilising toxic compounds (typically heavy metals) (Sune et al., 2005).

The high contents of ammonia and phosphate represent the decomposition phase of the organic substances, like in GW-6 and in GW-13. When the relation between the nitrogen derivatives and PO_4 are taken into consideration, all fertilisers used in the area are artificial (Figure 6) owing to the high PO_4 contents in all samples (McKenzie et al., 2001). Phosphate has a high tendency to be adsorbed on soil particles and is commonly transported with suspended sediments in surface runoff. In groundwater, phosphorus mobility is attenuated by its strong adsorption to soil particles.

AOX, a measure of dissolved chlorinated matter, is determined 0.25 mg/L (which is over the allowable limit according to Berlin drinking water standard (0.01 mg/L-www.stadtentwickling.berlin.de/umwelt/umweltatlas/ed204_04.htm) in the Porsuk River after treated process (oral communication with Sukru Aslan from Dokuz Eylul University).

Figure 6 The correlation between total nitrogen and PO_4



Aerial distribution of heavy metal contents in groundwater can be seen around the unsanitary landfill, wagon, and locomotive construction factory and abandoned abattoir vicinity (Figures 7 and 8). Samples collected from surface water and groundwater, near unsanitary landfill, have high Pb, Cr, Cd, and Mn. As can be seen from Figures 7 and 8, high concentration of heavy metals were concentrated in the similar area in accordance with nitrogen derivatives. Heavy metal contents of groundwater were also higher than allowable limits for drinking and domestic usage according to both Turkish Drinking Water Standard (TDWS, 1997) and WHO.

The correlation coefficients (r) of some chemical constituents in the waters of the study area for the wet and dry periods are given in Tables 3(a) and 3(b). The correlation coefficients between Nitrogen derivatives and sulphur-free chloride show weak but linear relationship that is expected owing to the prevailing of reductive environment.

Table 3(a) Correlation matrix of some chemical constituents for waters from study area by wet period (n = 15)

	B	*Free Cl*	*NO_2*	*NO_3*	*SSM*	*NH_3*	*NH_4*	*Sulphur*	*BOD*	*EC*
B	1.00	–	–	–	–	–	–	–	–	–
Free Cl	–0.05	1.00	–	–	–	–	–	–	–	–
NO_2	–0.02	0.00	1.00	–	–	–	–	–	–	–
NO_3	0.18	–0.05	0.16	1.00	–	–	–	–	–	–
SSM	0.10	0.37	–0.28	–0.20	1.00	–	–	–	–	–
NH_3	*0.46*	0.31	–0.11	0.10	*0.43*	1.00	–	–	–	–
NH_4	*0.46*	0.33	–0.09	0.14	*0.42*	*0.99*	1.00	–	–	–
Sulphur	0.19	*0.38*	*–0.27*	*0.40*	0.09	*0.30*	*0.38*	1.00	–	–
BOD	–0.21	0.33	–0.27	–0.04	–0.27	0.16	0.20	*0.55*	1.00	–
EC	*0.46*	–0.38	0.08	0.47	0.41	0.24	0.21	–0.29	–0.81	1.00

Table 3(b) Correlation matrix of some chemical constituents for waters from study area by dry period (n = 10)

	Free Cl	*NO_2*	*NO_3*	*Phenol*	*SSM*	*NH_3*	*NH_4*	*Sulphur*
Free Cl	1.00	–	–	–	–	–	–	–
NO_2	0.39	1.00	–	–	–	–	–	–
NO_3	–0.42	–0.05	1.00	–	–	–	–	–
Phenol	*0.40*	–0.20	0.12	1.00	–	–	–	–
SSM	–0.38	*0.65*	0.17	–0.80	1.00	–	–	–
NH_3	–0.05	–0.28	–0.08	*0.31*	–0.14	1.00	–	–
NH_4	–0.03	–0.27	–0.09	0.36	–0.16	*1.00*	*1.00*	–
Sulphur	*0.53*	*0.60*	–0.22	–0.18	0.33	*0.28*	*0.29*	1.00

Figure 7 Spatial distribution of Cd, Al, Cu, Zn, Cr contents in groundwater samples

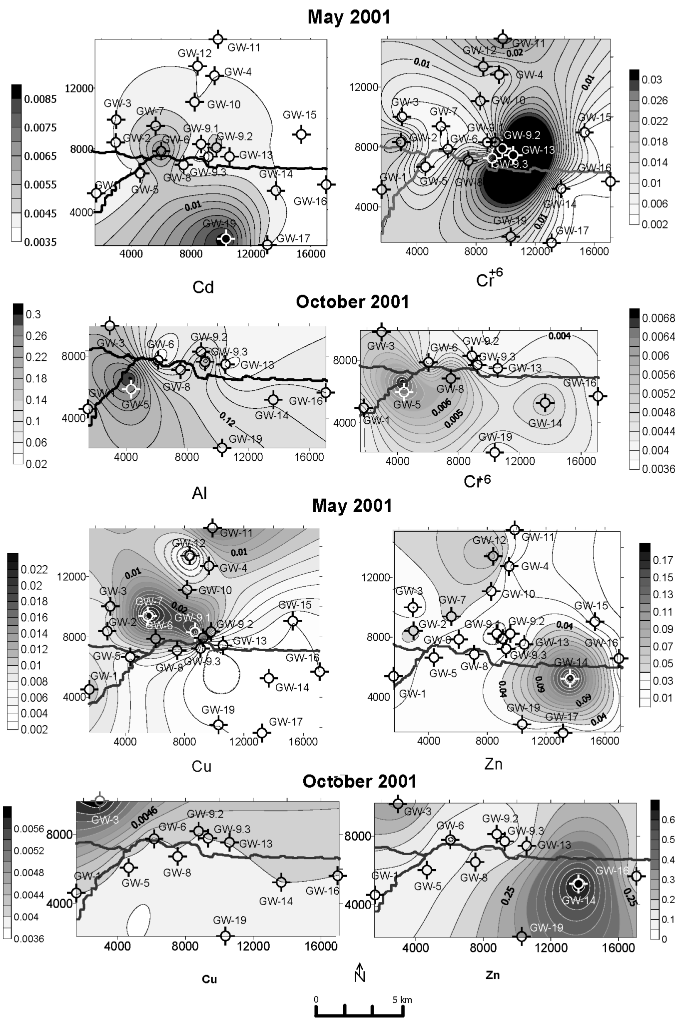
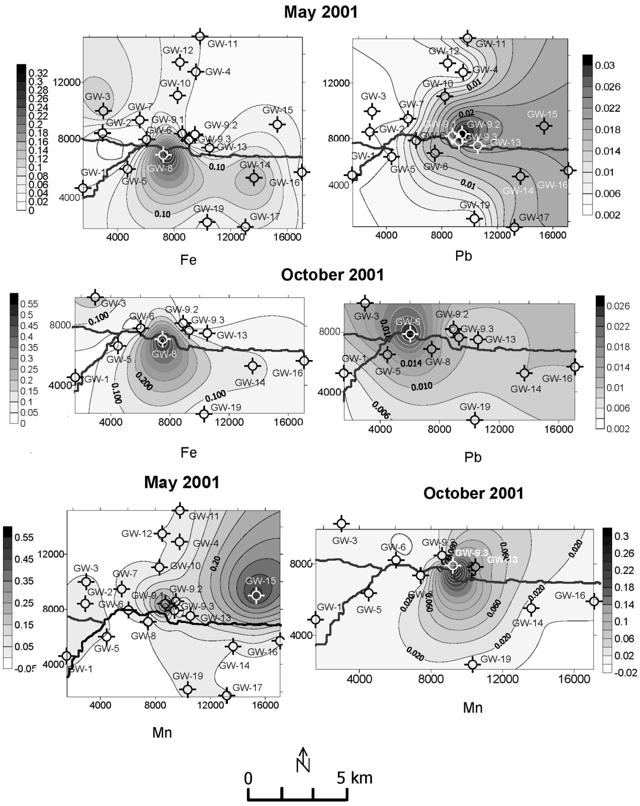


Figure 8 Spatial distribution of Fe, Pb, Mn contents in groundwater samples



5 Conclusions

The main source of the high nitrate content in the PRB is owing to the uncontrolled application of fertilisers for irrigation area. The common fertilisers applied liberally throughout the irrigation district are $(NH_4)_2SO_4$ and $(NH_4)_2NO_3$. Through a nitrification process in the presence of oxygen, ammonium is converted into nitrates according to $O_2 + \frac{1}{2}NH_4^+ = \frac{1}{2}NO_3^- + H^+ + \frac{1}{2}H_2O$ reaction (Freeze and Cherry, 1979). Thus, high nitrate content in groundwater is owing to contamination of the recharge to the aquifer by irrigation drainage and deteriorated sewage networks. Ammonium, ammonia, nitrite, SSM values are high in almost the entire region and exceed limit values of the Drinking Water Regulations. NH_4 is oxidised to NO_3 during processing at waterworks. NO_3 level is indeed raised, but is not disturbing at these low concentrations. The contributions of drinking water nitrate toward endogenous formation of N-nitrous compounds, which may cause cancer, reduce fertility and other chronic health effects (Ward et al., 2005). Nitrate accumulates on the top of soil surface and in the surface water bodies and spreads in the aquifer via groundwater flow. The low hydraulic conductivity owing to the presence of clay limits the flux of nitrate at GW-5, GW-11, GW-12 (northern part of Basin) where conditions are iron reducing.

The most serious contamination occurs in the central part of the city because of the high population, industrialisation, and dependence on groundwater. Expanded urbanisation and intensive changes in land use over past 40 years in the vicinity of Eskisehir has resulted in nitrate pollution of the water. N-fertiliser application needs to be controlled, especially in the recharge zone, together with the use of untreated River water for irrigation.

High concentration of N and P in groundwater of PRB is owing to river-groundwater interaction, besides intensive usage of fertilisers and pesticides. The river is hydraulically connected to the unconfined alluvium aquifer, thus contaminated water in the Porsuk River easily replenish the aquifer. Before 1998, groundwater in that of aquifer had been heavily used for irrigation and domestic purposes. Because of the pumping, the cone of depression intercepted the river, thus polluted river easily affected the groundwater quality. After municipal water treatment plant has worked, all these wells stopped to pump. Thus, groundwater level has arisen and river infiltration has been easier than before. Seasonal variations control the groundwater level and thus the direction of flow between the river and aquifer. When the hydraulic gradient of the aquifer is towards the river in winter season, groundwater discharges to the river, and the river becomes Effluent River. When the hydraulic gradient of the aquifer is a way from the river, the river becomes Influent River. The channel system can be hydraulically connected to the aquifer or have a leaking bed through which water can infiltrate to the subsurface. The overland flow also occurs when the rate of precipitation exceeds the infiltration capacity of local soil. The interaction between river and groundwater affects negatively on the groundwater quality, especially escalating in dry periods.

Phenol content of the treated water from Porsuk River has highly exceeded the allowable limits of TDWS for usage and drinking purposes. High phenol content is sourced from the chlorification of treated water and chlorated pesticides. Another problem in the area is originated from the high AOX (Adsorbable Organic Halogene) value in the treated water that caused by either the intensive chlorification of water in the Water Treatment Plant of Eskisehir and the wastewater effluent to the River from the Porcelain factories located in the catchment area of Porsuk River. The concentration of AOX in the Porsuk River is 0.25 mg/L, which exceeds the allowable limit for drinking water.

The leachate from this unsanitary waste disposal area discharged into the aquifer via subsurface infiltration. The spring GW-19 located in the downgradiant of the landfill is polluted by leachate in terms of organic and inorganic substances.

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References

Bakis, R. (1996) *The Investigation of the Environmental Effects of Waste Disposal in Eskisehir Region*, PhD Thesis, OGU, Graduate School of Natural, and Applied Science, Eskisehir.

Chen, J., Tang, C., Sakura, Y., Yu, J. and Fukushima, Y. (2005) 'Nitrate pollution from agriculture in different hydrogeological zones of the regional groundwater flow system in the North China', *Plain*, *Hydrogeology Journal*, Vol. 13, No. 3, pp.481–492.

Domenico, P.A. and Schwartz, F.W. (1990) *Physical and Chemical Hydrogeology*, John Wiley and Sons Inc., Canada, pp.579, 580.

Drever, J.I. (1997) *The Geochemistry of Natural Waters Surface and Groundwater Environments*, 3rd ed., Prentice-Hall, Upper Saddle River, NJ07458, New Jersey, pp.164–178.

DSI (1975) *Hydrogeological Investigation Report of Eskisehir ve Inönü Basins*, DSI Report, Ankara, No. 40, p.49 (original in Turkish).

EGDE, (1999) *The 1999 Results of the Eskisehir Branch of the General Directorate of Environment*, (unpublished data).

EGDE, (2000) *The 2000 Results of the Eskisehir Branch of the General Directorate of Environment*, (unpublished data).

EPA (2003) *Drinking Water Standards and Health Advisories*, Office of Water US EPA, Washington DC.

Fetter, C.W. (1999) *Contaminant Hydrogeology*, 2nd ed., Prentice-Hall, Upper Saddle River, NJ 07458, New Jersey, USA, pp.294–314.

Freeze, A.R. and Cherry, J.A. (1979) *Groundwater*, Pentice-Hall, Englewood Cliffs, NJ, USA.

Gozler, Z., Cevher, F., Ergul, E. and Asutay, J. (1996) *Geology of Southern and Middle Part of Sakarya*, MTA Publications No. 9973, Ankara, p.97 (in Turkish).

Kacaroglu, F. (1991) *Study of Contamination in the Eskisehir Basin*, PhD Thesis, Hacettepe University, FBE, Ankara, p.340 (original in Turkish).

Kacaroglu, F. and Gunay, G. (1997a) 'Groundwater nitrate pollution in an alluvium aquifer, Eskisehir urban area and its vicinity', *Environmental Geology*, Turkey, USA, No. 31, pp.178–184.

Kacaroglu, F. and Gunay, G. (1997b) 'Impacts of human activities on groundwater quality of an alluvial aquifer: a case study of the Eskisehir Plain', *Hydrogeology Journal*, Turkey, USA, Vol. 5, No. 3, pp.60–70.

McKenzie, M.J., Siegel, I.D., Patterson, W. and McKenzie, J.D. (2001) 'A geochemical survey of spring water from the main Ethiopian Rift Valley, Southern Ethiopia: implications for well-head protection', *Hydrogeology Journal*, Vol. 9, No. 3, Canada, pp.265–272.

Ölmez, E. and Yücel, B. (1985) *Geothermal Potential of Eskisehir and its Vicinity*, Directorate of Mineral Research and Exploration (MTA), Ankara, pp.1–18 (original in Turkish).

Özbek, T. (1976) *Geological and Hydrogeological Review of Eskisehir*, MTA Report, Ankara, No. 6374, pp.1–24 (original in Turkish).

Ozcelik, S. (1998) *Groundwater Potential and Pollution Problems in Eskisehir Basin (After 1995)*, Msc Thesis, Osmangazi University, Eskisehir, FBE, p.80 (original in Turkish).

Ren, S. (2002) 'Determining the mechanism of toxic action of phenols to tetrahymena pyriforms', *Environmental Toxicology*, Vol. 17, No. 2, pp.119–126.

Sune, V., Vila, X.S. and Carrera, J. (2005) 'Introductory review of specific factors influencing urban groundwater, an emerging branch of hydrogeology, with reference to Barcelona, Spain', *Hydrogeology Journal*, Vol. 13, No. 3, pp.522–533.

Su-Yapi (2001) *The Project of Water Management Plan of the Porsuk River Basin*, Term Report, Eskisehir, Chapter 12, pp.12–62 (in Turkish).

TDWS (1997) http://www.aquasu.com/sustandartlari.htm.

Vanloon, G.W. and Duffy, S.J. (2000) *Environmental Chemistry*, First Printed, Oxford University Press Inc., New York, pp.250–450.

Ward, M.H., Dekok, T.M., Levallais, P., Brender, J., Gulis, G., Nolan, B.T. and VanDerslice, J. (2005) 'Working report: drinking-water nitrate and health-recent findings and research needs', *Environmental Health Perspective*, Vol. 113, No. 11, pp.1607–1614.

Yuce, G., Pinarbasi, A., Ozcelik, S. and Ugurluoglu, D. (2006) 'Soil and water pollution derived from anthropogenic activities in the Porsuk River Basin, Turkey', *Environmental Geology*, Vol. 49, No. 3, pp.359–375.

Websites

URL: http://www.atsdr.cdr.gov/tfacts115.html.

URL: http://www.nsc.org/library/chemical/Phenol.htm.

URL: http://www.stadtentwickling.berlin.de/umwelt/umweltatlas/ed204_04.htm.