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## Soil and water pollution derived from anthropogenic activities in the Porsuk River Basin, Turkey

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**Abstract** This study aims to investigate the degree of the influence of contaminant sources on both the surface (Porsuk River) and groundwater in the Eskisehir plain, (Turkey) and to determine the changes in groundwater quality after the sewage system was started in 1998. For this purpose surface and groundwater samples were collected from various locations in the Eskisehir plain between May and October, 2001. The Porsuk River is already polluted in the upstream wastewater and by industries such as Nitrogen Fertilizer Factory, Sugar-beet Factory, and Magnesite Factory located around the city of Kutahya. This high-contaminated water forms an eutrophic environment which generates high phosphorus and nitrogen in downstream flow. Agricultural and industrial activities in the Eskisehir plain are an additional source

of the pollution of the Porsuk River. The study revealed that some trace elements, Pb, Cr, Mn, Fe, and Cd, are present in high concentrations both in the surface and groundwater besides extremely high quantities of phosphorus, nitrogen and sulfide compounds. In addition, analyses of samples also indicated that there are no considerable contaminations in terms of local pesticides. High concentration of Cd, N and S are found in the groundwater. On the basis of a detailed analysis of the groundwater in the Eskisehir plain, it is concluded that groundwater is not suitable for drinking according to Turkish standards, European Union Standards (EU) and World Health Organization (WHO).

**Keywords** Porsuk River · Diffuse pollution · Point source pollution · Chemical status

### Introduction

Both the surface and groundwater pollution by agricultural practices has been widely reported during the last two decades in many aquifers all over the world. This kind of pollution is usually exposed by high nitrate contents in groundwater and is related to over-fertilization of croplands in the recharge area of the aquifer. Other nutrients applied to croplands, such as phosphate or potassium, and organic compounds like pesticides, can be dissolved and mobilized from surface downwards to the water table through the vadose zone. However,

nitrate molecules from agricultural activities are highly mobile and play a major role in the pollution process.

Previous studies related to the area were made by DSI (1975) and Özbek (1976). General Directorate of State Hydraulic Works (DSI), the official authority for all water resources, investigated the effect of Porsuk River on the groundwater and the region in cooperation with UNDP and WHO. Ölmez and Yücel (1985) investigated the thermal water potential of the Eskisehir region and the thermal springs in Eskisehir city, and their effect on groundwater contamination. Additionally, Kaçaroğlu (1991, 1997a, b) investigated the nitrogen contamination

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in the groundwater from the Porsuk River. Bakis (1996), in his research entitled "The effect of Solid Waste on the Environment", mentioned the pollution created by the seeping waters from a waste deposition area rich in heavy metals. Özçelik (1998) researched the variations in groundwater quality after the completion of the city sewage system. Water samples from different parts of the Porsuk River were analyzed with respect to organic pollutants in 1999 by the Eskisehir branch of the General Directorate of Environment (EGDE) and this study is quoted as EGDE (1999) in this research.

This study aimed at researching the contamination degree of surface and groundwater by industrial and agricultural wastes including the municipal waste disposal area to the south of the city. In addition, the effect of Porsuk River, which is the main surface water from the center of Eskisehir city center carrying industrial contaminants into the groundwater was researched. This study is a part of the research project that supported by the Osmangazi University.

The followings are considered to be the possible contamination sources in the study: The discharge of the industrial waste waters by means of Porsuk River from Kütahya to Eskisehir cities. The high content of the contamination parameters, especially nitrogen and phosphorus, at the outlet of Porsuk dam. The dense industrial settlement in Eskisehir Centrum and the uncontrolled discharge of their wastes into the river. Irregular waste disposal area at Takahasan valley, 13 km south of the city, since 1987. The effects of use of the groundwater for agriculture in spite of the decrease in water quality.

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## Study area

The study was carried out in Eskisehir, NW of the Central Anatolia, Turkey, in an area of 500 km<sup>2</sup> between 39°41' 00"–39°32'30" latitudes and 30°22'46"–30°45'00" longitude. A continental climate, with long and cold winters and short and dry summers prevails in the area. It is rainy from November till May, and dry from June till October. According to the data of the Eskisehir meteorological station for the period of 1930–1990, the mean annual precipitation is 382 mm and the mean annual temperature is 10.90°C. The diurnal temperature range is 10–15°C.

A general geology map is given in Fig. 1. The oldest formations in the region are schist, crystalline limestone and ophiolitic *mélange* of the Triassic age. These formations outcropping at the south and north are tectonically in contact. Triassic formations are overlain by the conglomerates, marls, claystone, limestone, clays and tuffs of Eocene with an angular nonconformity. Tuffs, agglomerates and basalts of Lower Miocene and con-

glomerates, sandstones, marls, gypsum, marl-clay with gypsum and claystone of Upper Miocene, conglomerates, sandstones, tuffs, tuffites, basalts-andesites, and marl-claystone series of Pliocene overlie all older formations by nonconformably. Old and young alluviums are separated lithologically in the all well. Old alluvium of Pleistocene (Villafrancian) crops out at the edges of Eskisehir plan, formed of silt, clay, sand-fine sand, fine gravel, sandstone layers and gravels. The total thickness of old and young alluviums is 120 m, while the young alluvium in Quaternary consists of unconsolidated and actual river sediments with a thickness of 15 m.

The crystalline limestone, gabbros and serpentines of the *mélange* yield limited amounts of groundwater within their fracture systems. Conglomerate and sandstone levels of Eocene and limestone levels of Neogene also yield limited amounts of groundwater. Old and young alluviums are aquifers of importance.

The water table contour map were prepared by evaluating the water levels of drilled wells (Fig. 1). The groundwater is discharged into the Porsuk River, according to the flow line map at the left bank of Porsuk River. Although a corresponding trend is observed in higher altitudes, this situation disappears due to the intensive pumping by the wells drilled on the riverbank. On the right bank, groundwater recharges the river (Fig. 1).

Eskisehir is a rapidly growing industrialized metropolitan city. The main industries in the region are sugar-beet processing, alcohol, food processing, soft drinks, textiles, nitrogen fertilizer, wagon and locomotive manufacturing, earth products (brick, ceramics, porcelain etc.), metallic products, chemicals, electrical machines, wood, paper and plastic products. Agricultural activities in the Eskisehir region are quite intensive. About 60% of the land in the plain is irrigated. The major crops grown in the region are grains, sugar-beet, clover, sunflower, corn, vegetables, leguminous seeds, and fruits. Livestock breeding is an important aspect of agricultural production in the region. The animal products of the region are mostly from cattle, sheep, and goats (Kaçaroğlu 1997a). The population of the city is more than 500,000 according to the 2000 census. The rapid growth of the population and the industry in the city increases the water demand causing a reduction of water quality which is a serious problem.

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## Material and methods

Surface water samples were collected from six different locations of the Porsuk River and its tributaries (SW-1...SW-6). Groundwater samples were taken from 24 deep wells (GW-1...GW-24), and 12 soil samples (T-1...T-12) were picked from different depths in the plain

(Fig. 1). The sampling campaigns covered the period from May 2001 to October 2001. In addition, the EGDE (1999) data from the eight sections along the Porsuk River was also utilized for the comparison of the last and previous results.

The parameters of Turkish Drinking Water Standards were taken into consideration during the groundwater pollution surveys of the surface and groundwater during the wet and dry periods of 2001. The samples were collected according to the Turkish Standards for water sampling and analyzing methods.

Considering the probability of the absorption of the pollutants in the unsaturated zone, vertical continuous soil samples were taken. All elevations were determined by topographic survey. The sampling locations were selected downstream of the contaminating points. The surface water samples were taken directly from Porsuk River and irrigation channels and groundwater samples were collected from either springs or deep wells. Electrical conductivity (EC),  $t(^{\circ}\text{C})$ , pH and Eh values were measured in-situ by Schott Gerate handylab model instrument with  $\pm 0.5\%$  for EC and  $\pm 0.1$  for pH reading limits.

The sampling was carried out in May and October 2001. For sample collection one liter double tapped hard plastic and dark colored bottles were used. In order to prevent complex formation of heavy metals with oxygen, pH  $\leq 2$  conditions should be maintained. The heavy metal analyses were made by atomic absorption instrument. Since sulfur and nitrite could not be analyzed in field conditions, they were protected by adding zinc acetate solution and  $\text{HgCl}_2$ , respectively. For phenol, chemical oxygen demand (COD), ammonium-N, oil and grease analyses,  $\text{H}_2\text{SO}_4$  solution was added to reach pH  $\leq 2$  condition at  $+4^{\circ}\text{C}$ . For free chloride, biological oxygen demand (BOD), phosphorus, total dissolved solids (TDS), SSM, ammonia and nitrate analyses, the samples were kept at  $+4^{\circ}\text{C}$  and were analyzed within 1–2 h. TDS was measured by evaporation. COD and BOD were sampled and measured using standard methods (Greenberg et al. 1985).

Pesticide samples were analyzed at the Refik Saydam Central Poisons Research Laboratory by using instruments such as HPLC, GCL-ECD, GCL-TID, and GCL-FID. Soil samples were taken by hand augers from depth of 0–30 cm, 30–60 cm, 60–90 cm to 90–120 cm, and they were packed in 3-kg cloth sacks and sent to the Forestry District Directorate Soil and Water Laboratory in Eskisehir for analyses.

Groundwater levels were measured by electrical hand recorders with 1-cm sensitivity after pumping was stopped for periods long enough to reach static water level. Then, groundwater levels were calculated from the ground elevations measured by GPS and subtracting the water depth, and thus the water table contour map could be drawn.

## Results and discussion

Analysis results of 2001 wet and dry period sampling

### Groundwater

Depending on the routine analysis from the samples collected by applying the required standard parameters for sampling, the results are evaluated and discussed for the suitability of the groundwater for domestic and irrigation purposes in Table 1. The evaluations are based on the Turkish Drinking Water Standards (TDWS 1997) Code: TS-266 and Turkish Irrigation Water Standards (TIWS). Nitrite in GW-7 sample, nitrate in GW-9.2, boron, nitrite, phenol in GW-1; and boron in GW-19 and nitrate contamination are at maximum levels.

In the GW-5, phenol is high in addition to nitrite. GW-6 is high in boron. The groundwater samples show a decrease in boron values during dry period and no changes for  $\text{NO}_2$ ,  $\text{NO}_3$ , phenol, SSM,  $\text{NH}_3$ ,  $\text{NH}_4$ , sulphide, COD, organic N, oil and grease for drinking water limits. Samples collected in the dry period have extreme values of GW-13 and GW-19 for phenol (Table 1).

When the same samples were evaluated with respect to the water irrigation criteria (Table 1), the results were as follows: In Boron, GW-1, GW-9.1, GW-16 are within Class III and IV waters in the wet period and moved to Class II in the dry period. Other water samples were taken in Class III and IV. For free chlorine, GW-1, GW-3, GW-5, GW-6, GW-7, GW-8, GW-9.2, GW-10, GW-11, GW-12, and GW-15, which are in Class III and IV in the wet period, GW-1, GW-3, GW-5, GW-7, GW-9.2 show improvement in quality for the dry period. In GW-5 and GW-9.2, oil-grease is much above the standards. The increase is over 30% in GW-5 in the dry period. This may be due to increasing industrial activities. All samples are in Class IV for sulfur. The occurrence of the sulfur can be explained by the activities of bacteria (like *Desulfovibrio* and *Thiobacillus*) creating sulfur (Wedepohl 1974). For BOD, COD, TDS, phosphorus and SSM, the waters are in Class I and/or II. For  $\text{NO}_3$ , GW-1, GW-7, GW-8, GW-14 samples are in Class II and III (both in wet and dry periods). For  $\text{NO}_2$  and  $\text{NH}_4$ , most of the samples are in Class III and IV.

The results and evaluation of heavy metal contents of groundwater samples are given in Table 3. Samples collected from the groundwater, near the municipal waste deposition area (MWDA); carry high Pb, Cd, Cr and Mn elements. The changes in values are related to dilution caused by the precipitation. This situation is observed in the samples of GW-19, GW-5, GW-20, GW-7 and GW-3.

The two main factors, which control the mobility and toxicity, are the Eh-pH couple. The low pH value of GW-16 causes the reduction of  $\text{SO}_4$  to sulfide. Under

this acidic (low pH) condition, the heavy metal complexes, namely Cu, Fe, Mn and Zn, become mobile in aqueous solution (Drever 1997) and they are transferred into water when oxidized as seen in the case of GW-16.

### Surface water

The classification of water samples taken from the various sections of Porsuk River and its irrigation canals are given in Table 2. According to Table 2, the Porsuk River and its irrigation canals are not suitable for irrigation purposes.

The results and evaluation of heavy metal contents of surface water samples are given in Table 3. As can be seen in this Table, Mn and Fe contaminations are above the maximum limits for drinking water at most of the sampling points. The other heavy metal contaminations are generally either within or exceeding the recommended limits. The sample SW-7 collected from leachate of the MWDA has high contents of the elements, Pb, Cd, Cr and Mn.

The comparative results of the analysis of the surface water samples collected between the previous (EGDE 1999) and the 2001 surveys (in this study) from various sections of the Porsuk River are given in Fig. 2. The ammonium values are high in SW-2 and SW-4. When the old and new water analyses results of the Porsuk River are compared, an increase in COD and BOD are observed. This increase is due to the contribution of the contamination loads discharged from the Sugar Factory and the “Organized Industrial Area” as observed in sections SW-VI, SW-VII and SW-VIII. In section SW-VIII, NO<sub>2</sub> value decreases because of denitrification resulting from the increase in organic substances (Postma 1992). Besides the decrease in dissolved oxygen, the increase in NH<sub>3</sub> and in NH<sub>4</sub> confirms this thesis. The constant increase in P may be caused by the use of fertilizers and pesticides. Oil and grease value have increased in section SW-VIII. The increase of phenolic substances, boron, free chlorine and sulfur in section SW-VIII indicate the probability of the reductive environment.

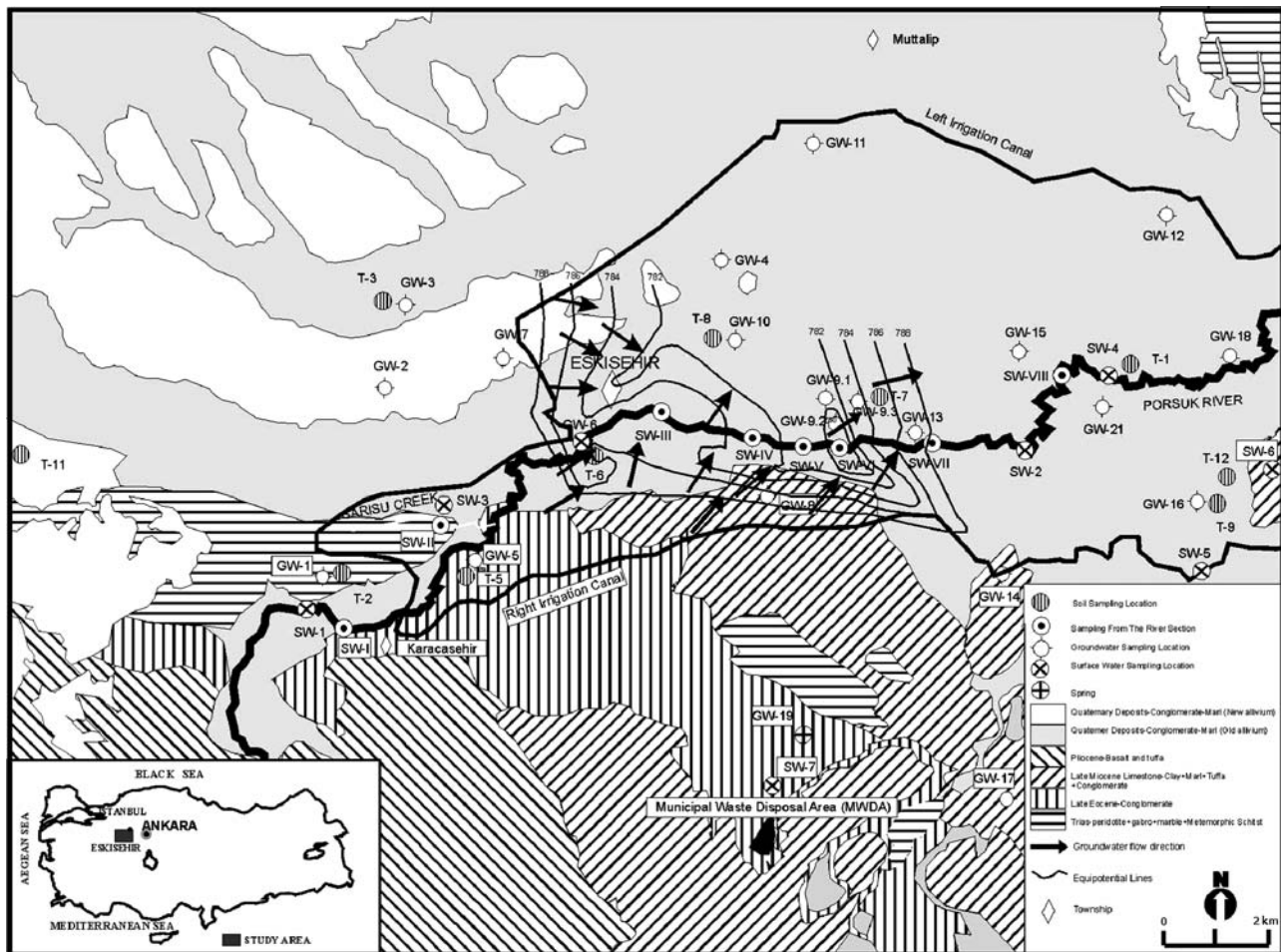


Fig. 1 Geological map and samples location in the study area

**Table 1** Evaluations of the analysis results of water sample according to the TDWS, 1997

Sample no	Sampling date	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)	
		Results	MCL	Results	MCL	Results	MCL	Results	MCL	Results	MCL	Results	MCL	Results	MCL	Results	MCL
GW-1	5/22/2001	2.10	OMCL	0.03	RL	0	RL	39.0	ORL			3.5	OMCL	4.65	OMCL	3.82	OMCL
	10/18/2001	0.55	RL	0.02	RL	3	OMCL	26.0	ORL			4.0	OMCL	7.95	OMCL	7.85	OMCL
GW-3	5/22/2001	0.70	RL	0.08	RL	4	OMCL	19.0	RL			5.0	OMCL	3.54	OMCL	2.90	OMCL
	10/19/2001			0.02	RL	4	OMCL	20.0	RL	0.12	OMCL	9.0	OMCL	2.20	OMCL	2.35	OMCL
GW-5	5/24/2001	0.75	RL	0.03	RL	6	OMCL	22.0	RL	0.01	OMCL	4.0	OMCL	3.47	OMCL	2.84	OMCL
	10/18/2001			0.01	RL	3	OMCL	15.0	RL	0.00	RL	5.0	OMCL	2.90	OMCL	2.85	OMCL
GW-6	5/23/2001	0.90	RL	0.04	RL	1	MCL	23.3	RL			5.0	OMCL	2.74	OMCL	2.17	OMCL
	10/18/2001													8.06	OMCL	7.98	OMCL
GW-7	5/23/2001	0.95	RL	0.05	RL	10	OMCL	56.0	OMCL			1.5	OMCL	3.40	OMCL	2.78	OMCL
	10/19/2001	0.39	RL	0.00	RL	4	OMCL	59.0	OMCL			9.0	OMCL	2.45	OMCL	2.46	OMCL
GW-8	5/23/2001	0.95	RL	0.05	RL	0	RL	44.0	ORL			4.5	OMCL	4.70	OMCL	3.57	OMCL
	10/19/2001	0.45	RL	0.04	RL	3	OMCL	37.0	ORL	0.16	OMCL	5.0	OMCL	3.61	OMCL	3.53	OMCL
GW-9.2	5/25/2001	1.35	ORL	0.07	RL	6	OMCL	18.0	RL	0.06	OMCL	3.0	OMCL	4.19	OMCL	3.22	OMCL
	10/19/2001	0.65	RL	0.00	RL	4	OMCL	15.0	RL	0.08	OMCL	10.0	OMCL	2.18	OMCL	2.11	OMCL
GW-10	5/25/2001	0.50	RL	0.05	RL	0	RL	38.0	ORL			2.0	OMCL	3.32	OMCL	2.71	OMCL
	10/19/2001	0.40	RL	0.06	RL	1	RL	17.0	RL			1.5	OMCL	2.83	OMCL	2.31	OMCL
GW-11	5/25/2001	0.60	RL	0.05	RL	2	OMCL	5.3	RL			2.0	OMCL	3.53	OMCL	2.67	OMCL
GW-12	5/25/2001	0.60	RL	0.05	RL	3	OMCL	20.0	RL			2.0	OMCL	4.25	OMCL	3.35	OMCL
GW-13	5/30/2001	0.75	RL	0.01	RL	3	OMCL	22.0	RL	7.70	OMCL	3.0	OMCL	6.73	OMCL	7.12	OMCL
	10/19/2001			0.01	RL	0	RL	15.8	RL			10.5	OMCL	4.36	OMCL	3.42	OMCL
GW-15	5/25/2001	0.90	RL	0.07	RL	3	OMCL	11.0	RL			1.5	OMCL	2.27	OMCL	1.64	OMCL
GW-16	5/25/2001	1.20	ORL	0.01	RL	3	OMCL	21.0	RL			3.0	OMCL	<0.02	ORL	<0.02	ORL
	10/19/2001	0.65	RL	0.02	RL	3	OMCL	20.2	RL			4.5	OMCL	3.31	OMCL	2.6	OMCL
GW-18	5/25/2001	0.55	RL	0.01	RL	4	OMCL	42.0	ORL			1.5	OMCL	2.02	OMCL	1.55	OMCL
GW-19	5/25/2001	0.55	RL	0.02	RL	2	OMCL	42.0	ORL			2.0	OMCL	1.01	OMCL	1.07	OMCL
	10/19/2001			0.00	RL	3	OMCL	42.0	ORL	6.70	OMCL	2.0	OMCL	2.76	OMCL	2.92	OMCL
DW-1	10/19/2001			0.70	MCL	4	OMCL	9.0	RL	6.60	OMCL	2.0	OMCL	2.06	OMCL	2.19	OMCL
GW-22	10/19/2001			0.02	RL	3	OMCL	5.0	RL	0.00	RL	8.0	OMCL	2.06	OMCL		

OMCL Over MCL; MCL Maximum Contamination Level; ORL Over RL; RL Recommended Level

**Table 2** Evaluations of the analysis results of water sample according to the TIWS, 1997

Sample no	Sampling date	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-gross Sulfide		COD		TDS		PO <sub>4</sub>		BOD				
		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	
SW-1	24.05.2001					0.17	IV	3.68	I			20	I									363	I							
SW-2	18.10.2001			0.03	II	2	IV	10	I			21	II																	
SW-4	24.05.2001	5.5	IV	0.09	IV	2	IV	4.4	I			16	I																	
SW-5	25.05.2001	0.85	II	0.19	IV	0	I	11.0	I			20.5	I																	
SW-6	25.05.2001	1.4	III	0.05	III	0	I	5.3	I			11	I																	
GW-1	22.05.2001	2.10	IV	0.03	III	0	I	39.0	II			3.5	I	4.65																
	18.10.2001	0.55	II	0.02	II	3	IV	26.0	II			4.0	I	7.95																
GW-3	22.05.2001	0.70	II	0.08	IV	4	IV	19.0	I			5.0	I	3.54																
	19.10.2001			0.02	II	4	IV	20.0	I	0.12		9.0	I	2.20																
GW-5	24.05.2001	0.75	II	0.03	III	6	IV	22.0	I	0.01		4.0	I	3.47																
	18.10.2001			0.01	I	3	IV	15.0	I	0.00		5.0	I	2.90																
GW-6	23.05.2001	0.90	II	0.04	II	1	IV	23.3	II			5.0	I	2.74																
	18.10.2001													8.06																
GW-7	23.05.2001	0.95	II	0.05	II	10	IV	56.0	III			1.5	I	3.40																
	19.10.2001	0.39	I	0.00	I	4	IV	59.0	III			9.0	I	2.45																
GW-8	23.05.2001	0.95	II	0.05	II	0	I	44.0	II			4.5	I	4.70																
	19.10.2001	0.45	I	0.04	I	3	IV	37.0	II	0.16		5.0	I	3.61																
GW-9.1	25.05.2001	1.35	III	0.07	III	6	IV	18.0	I	0.06		3.0	I	4.19																
	19.10.2001	0.65	II	0.00	II	4	IV	15.0	I	0.08		10.0	I	2.18																
GW-10	23.05.2001	0.5	I	0.05	I	0	I	38	II			2	I	3.32																
	19.10.2001	0.4	I	0.06	I	1	IV	17	I			1.5	I	2.83																
GW-11	23.05.2001	0.6	II	0.05	II	2	IV	5.3	I			2	I	3.53																
GW-12	30.05.2001	0.75	II	0.01	II	3	IV	20.0	I			2.0	I	4.25																
	19.10.2001			0.01	II	3	IV	22.0	I	7.70		3.0	I	6.73																
GW-15	25.05.2001	0.9	II	0.07	II	0	I	15.8	I			10.5	I	4.36																
	19.10.2001	1.20	III	0.01	III	3	IV	11.0	I			1.5	I	2.27																
GW-16	25.05.2001	0.65	II	0.02	II	3	IV	21.0	I			3.0	I	<0.02																
	19.10.2001	0.85	II	0.19	IV	0	I	11.0	I			20.5	I	1.84																
GW-17	25.05.2001	0.55	II	0.01	II	4	IV	20.2	I			4.5	I	3.31																
	19.10.2001	0.55	II	0.02	II	2	IV	42.0	II			1.5	I	2.02																
GW-19	25.05.2001	0.55	II	0.00	II	3	IV	42.0	II	6.70		2.0	I	1.01																
	19.10.2001			0.70		4		9.0		6.60		2.0	I	2.76																

I Very good; II Good; III Bad; IV Very bad

<sup>a</sup>The class is based on Turkish Irrigation Water Standard

**Table 3** Evaluations of heavy metals analysis

Sample no	Sampling date	Total zinc (mg/l)	Total lead (mg/l)	Total crom (mg/l)	Total manganese (mg/l)	Total iron (mg/l)	Total copper (mg/l)	Total mercury (mg/l)	Total cadmium (mg/l)	Total aluminium (mg/l)	Total arsenic (mg/l)
Results of groundwater samples											
<i>RL</i>		<i>0.1</i>	<i>0.01</i>	<i>0</i>	<i>0.02</i>	<i>0.05</i>	<i>0.1</i>	<i>0</i>	<i>0</i>	<i>0.05</i>	<i>0</i>
<b>MCL</b>		<b>5</b>	<b>0.05</b>	<b>0.05</b>	<b>0.05</b>	<b>0.2</b>	<b>3</b>	<b>0.001</b>	<b>0.005</b>	<b>0.2</b>	<b>0.05</b>
GW-1	5/26/2001	0.034	<0.005	0.017	<0.005	0.04	0.011	<0.005	<0.005		
	10/18/2001	0.042	<0.005	<0.005	<0.005	0.02	<0.005	<0.0005	<0.005	0.158	<0.003
GW-2	5/25/2001	0.045	<0.005	0.021	<0.005	0.02	0.009	<0.005	<0.005		
GW-3	5/25/2001	0.019	<0.005	0.005	<0.005	0.12	0.009	<0.005	<0.005		
	10/19/2001	<i>0.321</i>	<i>0.014</i>	0.005	0.008	<i>0.19</i>	0.006	<0.0005	<0.005	0.187	<0.003
GW-4	5/26/2001	0.019	<0.005	0.012	<0.005	<0.05	0.009	<0.005	<0.005		
GW-5	5/25/2001	0.023	<0.005	<0.005	<0.005	0.02	0.007	<0.005	<0.005		
	10/18/2001	0.087	<i>0.013</i>	0.007	<0.005	<0.05	<0.005	<0.0005	<0.005	<b>0.308</b>	<0.003
GW-6	5/25/2001	0.021	<i>0.012</i>	<0.005	<0.005	0.03	0.013	<0.005	<b>0.007</b>		
	10/18/2001	0.044	<i>0.028</i>	<0.005	<0.005	<0.05	<0.005	<0.0005	<0.005	0.02	<0.003
GW-7	5/27/2001	0.045	<0.005	<0.005	<0.005	0.05	0.024	<0.005	0.005		
GW-8	5/26/2001	0.023	<i>0.017</i>	<i>0.021</i>	<0.005	<b>0.34</b>	0.008	<0.005	<0.005		
	10/19/2001	<i>0.107</i>	<i>0.014</i>	<i>0.006</i>	0.009	<b>0.6</b>	<0.005	<0.0005	<0.005	0.092	<0.003
GW-9.1	5/26/2001	0.026	<i>0.035</i>	<i>0.014</i>	<0.005	0.04	0.011	<0.005	0.005		
GW-9.2	5/25/2001	0.012	<i>0.023</i>	<i>0.006</i>	<b>0.367</b>	0.03	0.022	<0.005	<0.005		
	10/19/2001	0.062	0.007	<0.005	<i>0.037</i>	0.03	<0.005	<0.0005	<0.005	0.105	<0.003
GW-9.3	5/25/2001	0.024	<i>0.019</i>	<i>0.017</i>	<b>0.086</b>	0.03	<0.005	<0.005	<0.005		
	10/19/2001	0.081	<i>0.011</i>	<0.005	<b>0.323</b>	<i>0.06</i>	<0.005	<0.0005	<0.005	0.174	<0.003
GW-10	5/25/2001	0.039	<i>0.013</i>	<i>0.012</i>	<0.005	0.05	0.01	<0.005	<0.005		
GW-11	5/25/2001	0.029	<i>0.014</i>	<i>0.028</i>	<0.005	0.04	0.017	<0.005	<0.005		
GW-12	5/27/2001	0.074	<0.005	<i>0.017</i>	<0.005	0.05	<0.005	<0.005	<0.005		
GW-13	5/26/2001	0.029	<i>0.022</i>	<b>0.083</b>	<b>0.093</b>	0.04	<0.005	<0.005	<0.005		
	10/19/2001	<i>0.124</i>	0.009	<0.005	<b>0.105</b>	<i>0.07</i>	<0.005	<0.0005	<0.005	0.031	<0.003
GW-14	5/27/2001	<i>0.184</i>	<i>0.017</i>	<0.005	<0.005	<i>0.15</i>	<0.005	<0.005	<0.005		
	10/19/2001	<i>0.71</i>	0.01	<i>0.005</i>	<0.005	<i>0.12</i>	<0.005	<0.0005	<0.005	0.097	<0.003
GW-15	5/25/2001	0.012	<i>0.021</i>	<0.005	<b>0.487</b>	0.05	<0.005	<0.005	<0.005		
GW-16	5/26/2001	0.01	<i>0.02</i>	<0.005	<0.005	0.03	<0.005	<0.005	<0.005		
	10/19/2001	0.297	<i>0.038</i>	<0.005	<b>0.053</b>	<b>1.34</b>	<i>0.219</i>	<0.0005	<0.005	0.134	<0.003
GW-17	5/25/2001	0.013	<i>0.017</i>	<0.005	<0.005	<i>0.08</i>	<0.005	<0.005	<0.005		
GW-19	5/27/2001	0.031	<0.005	<i>0.017</i>	<0.005	0.05	<0.005	<0.005	<b>0.009</b>		
	10/19/2001	<i>0.315</i>	0.006	<0.005	<0.005	0.05	<0.005	<0.0005	<0.005	0.139	<0.003
GW-20	5/26/2001	<i>0.827</i>	<i>0.023</i>	<i>0.025</i>	<b>0.614</b>	<b>5.69</b>	<i>0.108</i>	<0.005	<0.005		
GW-21	10/19/2001	0.044	0.005	<0.005	0.015	<b>0.21</b>	<0.005	<0.0005	<0.005	<b>0.325</b>	<0.003
GW-22	10/19/2001	0.031	<0.005	<0.005	<0.005	<0.05	<0.005	<0.0005	<0.005	0.118	<0.003
Results of surface water samples											
<i>RL</i>		<i>0.1</i>	<i>0.01</i>	<i>0</i>	<i>0.02</i>	<i>0.05</i>	<i>0.1</i>	<i>0</i>	<i>0</i>	<i>0.05</i>	<i>0</i>
<b>MCL</b>		<b>5</b>	<b>0.05</b>	<b>0.05</b>	<b>0.05</b>	<b>0.2</b>	<b>3</b>	<b>0.001</b>	<b>0.005</b>	<b>0.2</b>	<b>0.05</b>
SW-1	5/25/2001	0.017	<i>0.017</i>	<0.005	<i>0.039</i>	<i>0.19</i>	0.08	<0.005	0.005		
	10/18/2001	0.06	<i>0.012</i>	<0.005	<b>0.054</b>	<b>0.27</b>	<0.005	<0.0005	<0.005	<b>0.319</b>	<0.003
SW-2	5/25/2001	0.032	<0.005	<0.005	<b>0.063</b>	<i>0.1</i>	0.013	<0.005	0.005		
SW-3	5/27/2001	0.065	<0.005	0.024	<i>0.027</i>	<b>0.32</b>	0.015	<0.005	<0.005		
	10/19/2001	0.1015	<i>0.013</i>	<0.005	0.014	<i>0.15</i>	<0.005	<0.0005	<0.005	<b>0.219</b>	<0.003
SW-4	10/19/2001	<i>0.325</i>	<i>0.016</i>	0.012	<b>0.108</b>	<b>0.47</b>	0.013	<0.0005	<0.005	<b>0.448</b>	<0.003
SW-7	5/25/2001	0.053	<b>0.055</b>	<b>0.083</b>	<b>0.141</b>	0.05	0.015	<0.005	<b>0.016</b>		
SW-III	10/19/2001	0.075	0.008	<0.005	0.008	<0.05	<0.005	<0.0005	<0.005	0.142	<0.003
SW-VI	10/19/2001	0.075	<i>0.011</i>	<0.005	<b>0.08</b>	<b>0.37</b>	0.01	<0.0005	<0.005	<b>0.343</b>	<0.003
SW-VII	10/19/2001	0.039	0.009	<0.005	<b>0.07</b>	<i>0.19</i>	0.01	<0.0005	<0.005	<b>0.298</b>	<0.003
DW-1	10/19/2001	<i>0.292</i>	0.006	<0.005	0.006	<0.05	<0.005	<0.0005	<0.005	0.097	<0.003

Bolds are represented as over the maximum contamination level (MCL)

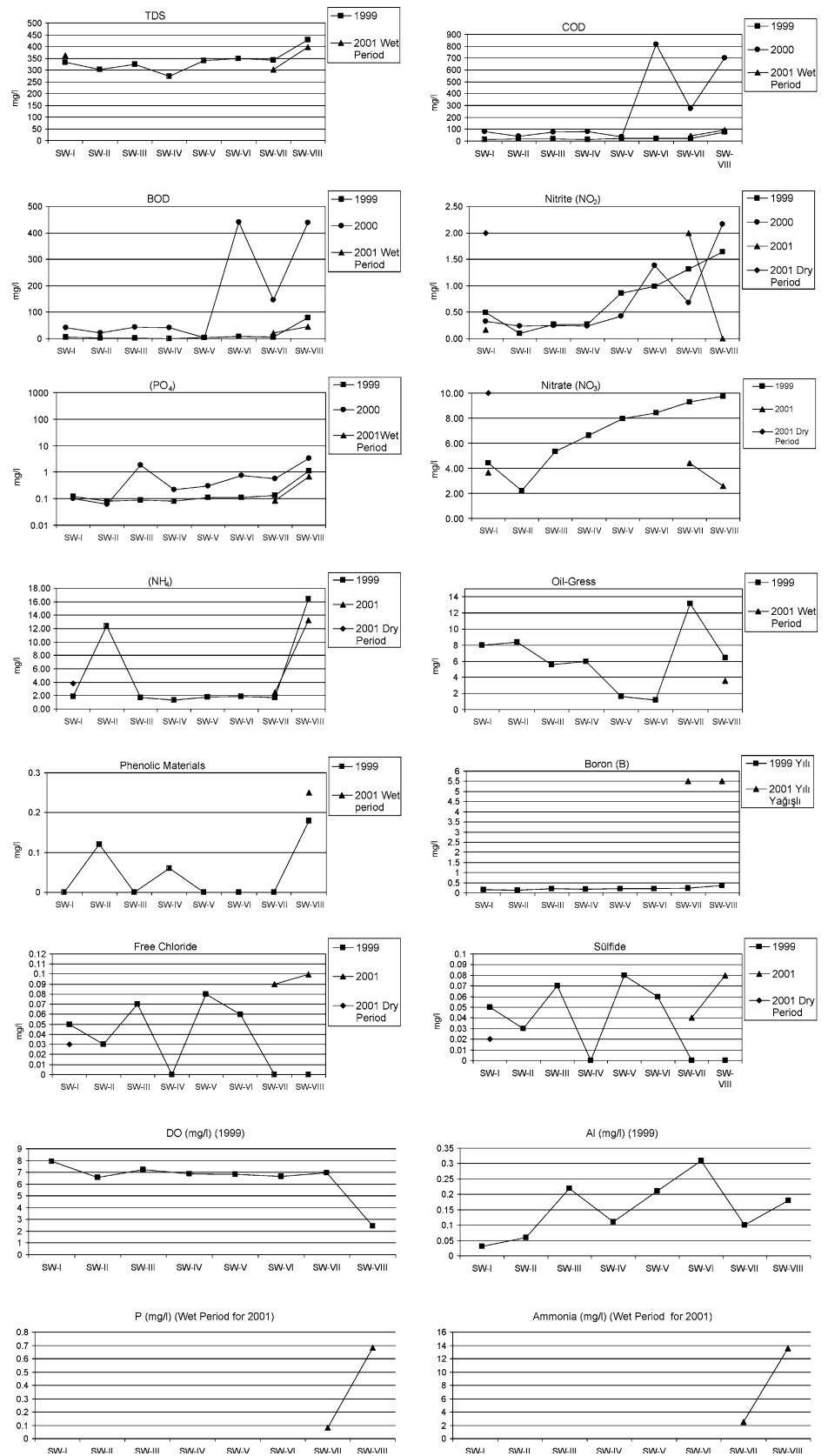
Italics are represented as over the recommended level (RL)

According to Turkish Drinking Water Standarts (Code No: TS/266)

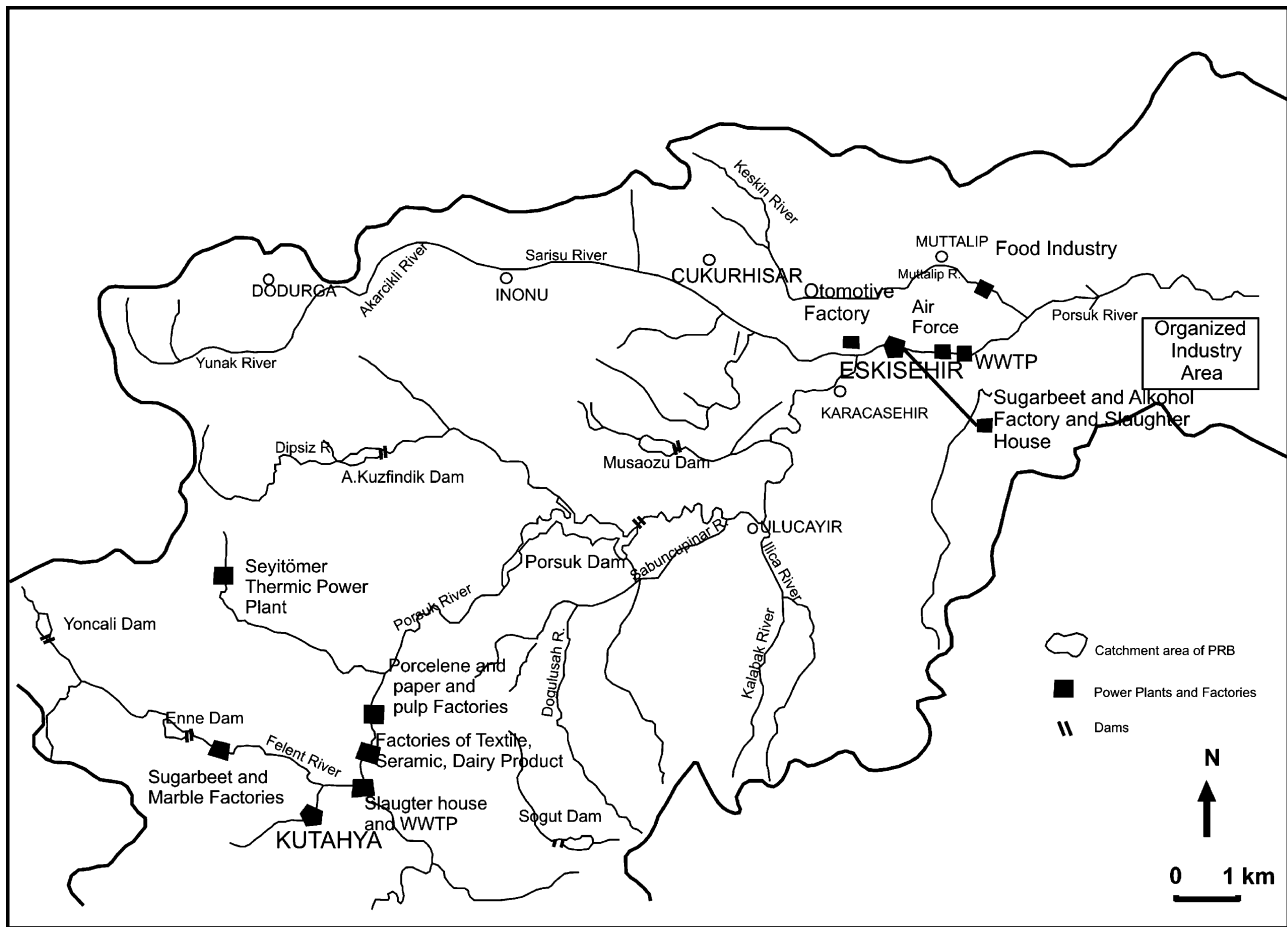
Possible contamination sources of the Porsuk River are shown in Fig. 3. Especially for Kutahya part, the wastewater of the Sugar Factory is discharged into the Felent River and BOD is 17.95 mg/l. The slaughterhouse

of Kütahya city also discharges its sewage water into the Felent River from its insufficient wastewater treatment plant. The discharges of the wastewaters from many factories and especially from Seyitömer Thermal Electric

**Fig. 2** Analyses results of samples taken at different times from the different locations at Porsuk River







**Fig. 3** Plants which discharge their waste water into Porsuk River in Kutahya and Eskisehir Region marble plant, sugar beet plant, slaughterhouse, thermic power plant, textile plant, food industry...etc

Power Plant contribute to the pollution of the river. This polluted water reaches the Porsuk Dam reservoir. The existence of high nitrogen and phosphorus at the outlet of Porsuk Dam are sourced from decomposed organic substances with sediments from the hypolimnion zone of the reservoir (Drever 1997). Improvements are observed in water quality in terms of nitrogen and phosphorus contents except in the stretch from the outlet of Porsuk dam until the Eskisehir city center. This improvement in water quality is sustained until the Eskisehir Sugar Factory sampling station (SW-IV) in the wet period of 2001. However, from this point (SW-IV) the quality of the Porsuk River water becomes Class IV irrigation water according to TIWS, 1997. This indicates that the wastewater treatment plant of the Sugar Factory does not work properly. This situation can be obviously understood by increase in  $\text{NH}_3$ ,  $\text{NH}_4$ , phenol,  $\text{NO}_2$ , B, SSM, free chlorine and Mn values in the samples taken from GW-9.2 well in the Sugar Factory (Tables 2, 3). By taking the wastewaters of slaughterhouse and The Air Force and Maintenance Center, the water quality of the

river becomes worse at the SW-VI point, which is the last sampling point on the Porsuk River.

#### *Soil samples*

The soil samples (T) collected by hand augers from various depths were analyzed and the results are given in Table 4. The aim was to investigate the heavy metals and pesticide adsorption capacity of soil before reaching the aquifer. According to the soil analysis, except in T-7b, the high Ca and Mg indicate a good permeability in soil near the Sugar Factory. High Fe and Mn in T-7a and T-7b are from the activity of the Sugar Factory. The EC, S, B, OM,  $\text{P}_2\text{O}_5$ , Fe, Mn, Pb, Zn values are high in T-7a and T-7b and in GW-9.1 and GW-9.2 wells located in the same area. Mn, B,  $\text{NH}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$  and Pb values are relatively high. The boron value is high in SW-VIII (SW-4) and low in T-1 sample. This indicates that the high boron content in Porsuk River water is not from the soil but from the pollution load derived from Organized Industrial Region. In T-2 soil sample, OM and

**Table 4** Soil analysis results taken from different depths (ppm)

Soil sample no and depth interval (cm)	Physical parameters					Soil types	Fe	Mn	Zn	Cu	Pb	P <sub>2</sub> O <sub>5</sub>	S	Ca	Mg	K	Na	T. lime (%)	Org. material (%)	T. nitrogen (%)	EC $\mu$ S/cm	Boron ppm
	pH	Sand %		Clay %																		
		Dust %																				
T-1 50-70	8.00	35.19	22.63	42.18	Clay	0.44	0.22	0.22	0.22	2.31	45	28	5781	2421	638	859	11.74	1.85	0.11	410	0.00	
T-1 70-90	8.00	33.54	26.81	39.65	Loam	0.33	0.11	0.22	0.22	4.15	5	204	5390	2989	349	764	18.64	1.03	0.06	900	0.11	
T-1 90-120	8.00	36.79	37.10	26.11	Loam	0.32	0.54	0.21	0.11	5.80	5	197	4468	2658	322	794	14.52	0.45	0.04	1110	0.00	
T-2 0-10	8.00	58.34	26.60	15.07	Sandy loam	0.53	2.95	0.74	9.68	6.42	60	23	5284	1231	800	189	3.75	4.24	0.19	770	2.11	
T-2 0-30	8.00	61.75	21.06	17.19	Sandy loam	0.21	0.21	0.42	0.84	5.79	14	6	6392	891	527	253	3.75	1.65	0.16	570	1.03	
T-2 80-100	8.10	60.38	18.21	21.41	Sandy loam	0.42	1.05	0.63	1.58	3.27	17	30	6395	1022	421	253	5.25	2.11	0.08	590	0.58	
T-3 0-50	8.00	56.72	26.59	16.69	Sandy loam	0.10	0.10	0.31	0.20	6.34	26	57	4066	583	522	501	5.82	1.09	0.04	450	0.00	
T-4 50-80	7.80	43.00	24.76	32.24	Loam	0.64	0.11	0.43	0.11	4.04	85	245	4777	1472	1531	425	10.59	1.90	0.12	2000	0.04	
T-5 0-40	7.80	80.29	14.88	4.84	Sandy loam	0.90	0.78	0.45	0.22	6.16	59	109	9623	3943	358	224	7.17	20.36	0.31	720	1.93	
T-6 0-10	7.80	53.57	22.66	23.77	Sandy loam	0.53	1.81	2.24	1.92	4.47	124	50	5478	1082	1533	266	11.36	8.09	0.32	770	0.42	
T-7a 0-10	7.30	64.57	22.71	12.72	Sandy loam	14.15	38.31	7.02	6.40	11.36	66	3030	8268	102	743	743	15.43	7.70	0.33	14390	2.02	
T-7b 0-20	8.50	18.58	62.20	19.22	Dusty loam	11.75	0.63	0.94	5.88	5.35	2378	3950	3637	5057	1595	1616	74.65	8.61	0.69	24670	0.05	
T-8 0-50	7.80	23.40	26.54	50.06	Clay	0.97	1.62	0.54	0.54	4.86	148	313	5391	1738	865	476	11.53	5.89	0.35	1950	0.30	
T-8 50-80	7.80	27.51	24.45	48.03	Clay	0.33	0.33	0.33	0.11	2.71	131	233	6986	1142	368	325	13.10	1.63	0.13	1340	0.23	
T-8 80-100	7.80	22.21	25.29	52.50	Clay	0.54	0.11	0.33	0.43	0.76	72	189	7351	967	239	326	13.14	1.21	0.05	1250	0.22	
T-9 30-50	8.00	35.03	24.08	40.89	Clay	0.32	0.32	0.21	0.11	6.51	42	27	4098	700	213	854	26.57	1.62	0.16	570	0.20	
T-9 60-90	8.00	37.20	15.53	47.27	Clay	0.75	0.11	0.21	0.11	5.01	39	16	5542	610	149	683	30.36	1.23	0.09	490	0.00	
T-9 90-120	8.00	31.14	17.58	51.28	Clay	0.11	0.21	0.32	0.11	6.05	22	70	5330	681	892	446	35.49	1.27	0.12	470	0.00	
T-10a 0-10	7.90	48.99	28.90	22.11	Sandy loam	0.65	3.48	0.44	0.22	3.05	70	1	8089	566	609	163	21.68	2.54	0.15	360	0.00	
T-10a 0-30	8.00	45.04	16.93	38.03	Sandy clay	0.11	0.11	0.44	0.11	2.99	38	1	8440	627	532	155	18.93	2.60	0.16	290	0.00	
T-10a 60-80	7.90	43.00	19.09	37.91	Loam	0.44	0.11	0.33	0.22	5.96	58	1	8276	630	508	166	19.65	2.66	0.16	330	0.00	
T-27b 0-10	7.90	50.94	26.85	22.21	Sandy loam	0.87	0.33	0.11	0.11	6.34	25	19	6526	1653	634	164	10.11	2.09	0.12	470	0.53	
T-27b 0-30	8.00	43.94	24.86	31.20	Loam	0.66	0.11	0.22	0.11	4.52	15	15	7032	1924	551	242	10.97	1.68	0.10	380	0.45	
T-27b 60-80	8.00	52.15	21.16	26.69	Sandy loam	0.22	0.22	0.22	0.11	4.50	18	7	6791	2270	417	263	12.49	1.56	0.10	380	0.08	
T-11 0-40	8.10	43.85	16.63	39.52	Loam	0.22	0.11	0.44	0.22	3.16	90	17	5064	1478	392	588	9.29	2.32	0.11	380	0.00	
T-11 50-70	8.00	43.50	18.92	37.58	Loam	0.44	0.11	0.44	0.22	3.61	45	22	5357	1329	329	591	14.81	1.28	0.08	430	0.23	
T-12 50-70	8.10	26.74	20.33	52.93	Clay	0.44	0.66	0.22	0.11	0.11	88	50	4851	2046	570	1041	19.49	1.88	0.11	710	0.00	

N are relatively high while in the GW-1 sample N compounds are also found in high amounts. In the T-6 soil sample organic material and  $P_2O_5$  values are high and in GW-6 sample, P is also relatively high. In T-8 soil sample,  $P_2O_5$  and S values are high, and BOD is high in GW-10 sample.

## Evaluation of analysis results

### Groundwater

Essentially  $NO_2$ ,  $NO_3$ ,  $NH_3$  and  $NH_4$  values are high in the groundwater samples collected from the investigation area. In shallow aquifer, under sufficient drainage conditions, the  $NO_3$  content increases with the thickness of the unsaturated zone (Postma 1992). If the drainage is weak and permeability is low, the denitrification process occurs and  $NO_3$  decrease. In Fig. 4, increase in  $NO_3$  with the thickness of the unsaturated zone is indicated. During the dry period, the  $NO_3$  concentration in GW-5 decreased 35% compared to the wet period due to the oxygen consumption, i.e. denitrification.

The increase in the  $NO_3$  content was observed in waters sampled from the deep wells (Fig. 5). The increase in  $NO_3$  and decrease in  $NH_3$ ,  $NH_4$  and sulfide from the wet to dry periods of 2001 in GW-16 show that nitrification occurs. In GW-1, GW-6 and GW-13, there is an increase in  $NH_4$ ,  $NO_2$ ,  $NH_3$  and a decrease in  $NO_3$  values. This can be explained by the denitrification process. The increase in organic substances can bring about the ammonification and denitrification process (Böhlke 2002). As the organic substance amount increases,  $NO_3$  decreases and  $NH_3$  increases (ammonification) (Allen and Chapman 2001; Postma 1992). Nitrogen proteins and amino acids take place in ammonification process. When organic substances are decomposed under the effects of water and soil,

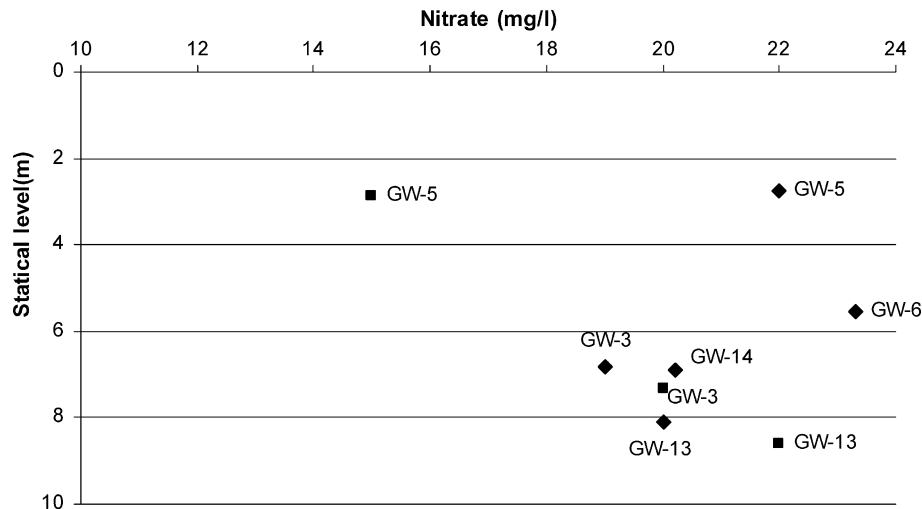
nitrogen leaves the environment as  $NH_4$  or  $NH_3$  related to pH (Vanloon and Duffy 2000). In Fig. 6, the increase in  $NH_3$  and  $NH_4$  can be observed together with organic material except for GW-6, GW-11, GW-16, and GW-19. It can be said that in GW-6, GW-11, GW-16, GW-19, some other oxygen consuming processes may occur such as in the oxidation of pyrite. While nitrate has mobility with biological control,  $NH_3$  is immobilized within geochemical and biological processes (Vanloon and Duffy 2000) Thus,  $NH_4$  can be preserved for a long time in the environment.

In the wells, GW-1, GW-7, GW-10, with high  $NO_3$  contents, the sand and gravel layers are predominant. However, clay dominant layers may create an oxygen free environment by capturing the organic substances, which causes denitrification. This is observed in GW-1, GW-6 and GW-13.

Dissolved P is found as phosphoric acid ( $H_3PO_4$ ) in the waters and decomposes as orthophosphate ( $H_2PO_4$ ). Dissolved phosphorus is quickly absorbed by the soil and has a low mobility in groundwater (Fetter 1999). Samples from GW-1, GW-3, GW-5, GW-6, GW-7, GW-15, and GW-18 have high phosphorus contents. There are two sources for the phosphorus of surface waters: the wastes coming from detergent and soap factories, and anthropogenic substances taken away by the sewage system. The latter is more significant for the Eskisehir plain (Vanloon and Duffy 2000). The high contents of ammonia and phosphate represent the decomposition of the organic substances, as seen in GW-6 and in GW-13.

The other pollutant, phenol, may be sourced from chlorine pesticides and industrial wastes (Domenico and Schwartz 1990). The phenol contents (between 0.01 and 7.7 mg/l) are much higher than the value allowed for drinking water ( $5.0 \times 10^{-4}$  mg/l) in GW-3, GW-5, GW-8, GW-9.2, GW-13, GW-19 and DW-1 (Table 2).

**Fig. 4** The thickness of unsaturated zone versus nitrate variations (square Dry Period, diamond Wet Period)



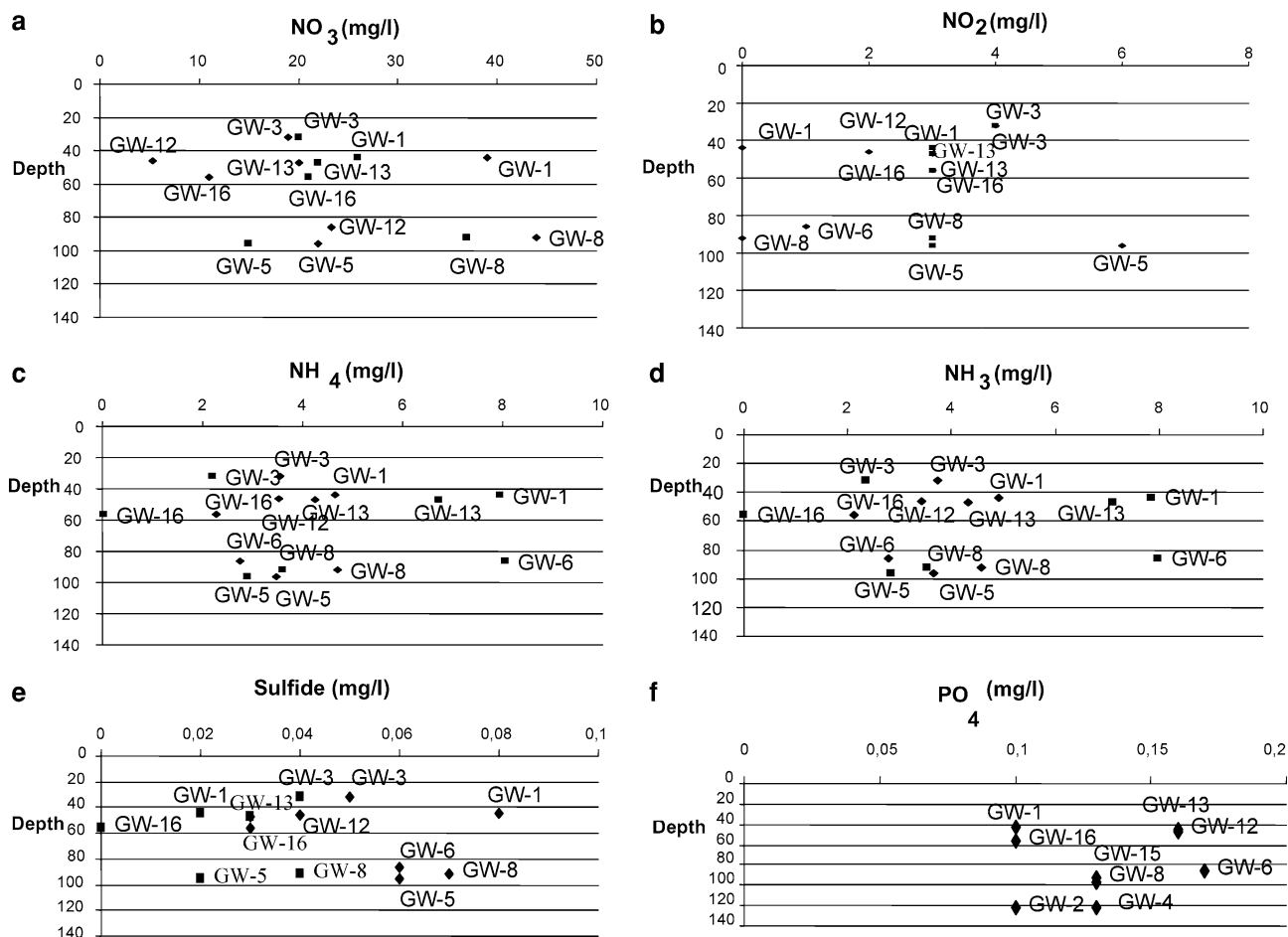


Fig. 5 Last filter depths of Wells versus NO<sub>3</sub> (a), NO<sub>2</sub> (b), NH<sub>4</sub> (c), NH<sub>3</sub> (d), Sulfide (e), PO<sub>4</sub> (f) (mg/l)

The phenol content in DW-1 is among the highest and this is very harmful for drinking and domestic usage. The possible sources of this high phenol content are chlorine pesticides and industrial wastes. Another concern is high toxic adsorbable organic halogen (AOX) caused by the intensive chlorination effect (Barber et al. 1995).

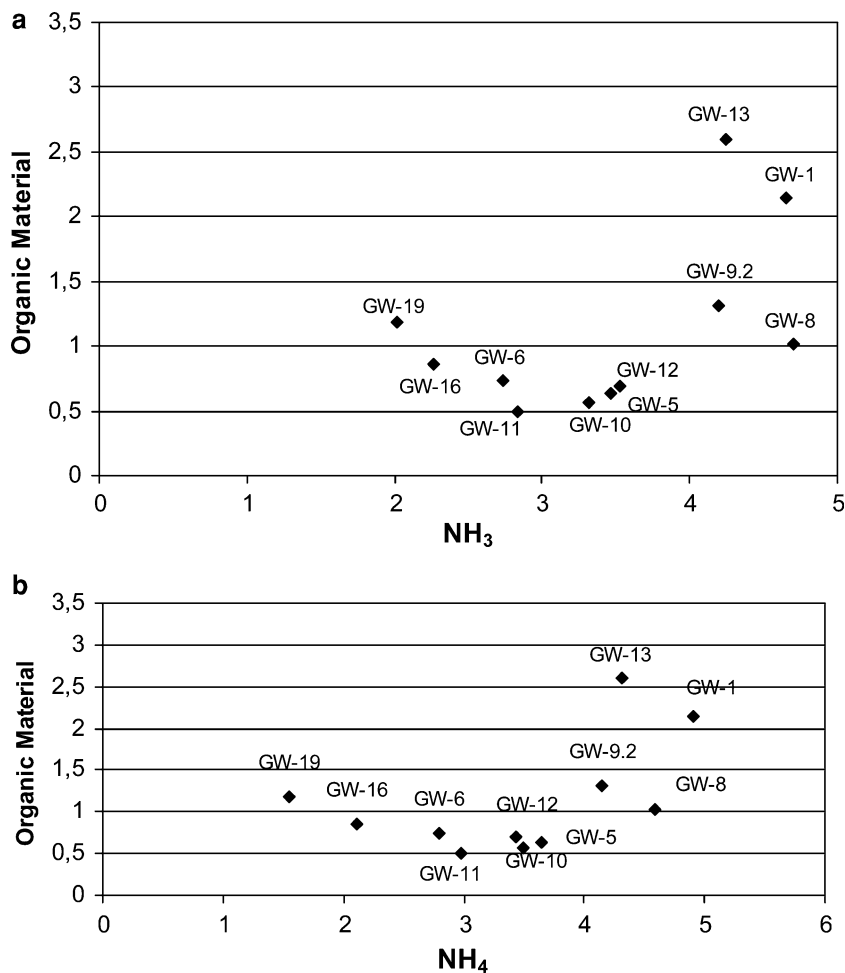
The spatial distribution of the seasonal nitrate and nitrite concentrations of the groundwater in the Eskisehir basin are presented by concentrations contour maps in Fig. 7. The contours allow identification of possible nitrogen problem areas and their related sources. A close examination of the nitrate concentration contour maps (Fig. 8) reveals that the highest nitrate concentrations were observed in the central eastern parts of the region. These areas coincide with the densely populated and industrialized and unsewered parts of the city. Also, nitrate concentrations of water from wells, in general, are higher than those of water from the Porsuk River. Agricultural impact with the application of nitrogen containing fertilizers such as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in

irrigation has been mostly associated with nitrate pollution in groundwater.

Cr was observed in GW-13 sample and probably had an industrial origin. Aluminum content of groundwater sample GW-5 is high.

The analyzed pesticide species are chlorpyrifos methyl (C<sub>7</sub>H<sub>7</sub>Cl<sub>3</sub>NO<sub>3</sub>PS), endosulphan (C<sub>9</sub>H<sub>6</sub>Cl<sub>6</sub>O<sub>3</sub>S), deltamethrin (C<sub>22</sub>H<sub>19</sub>Br<sub>2</sub>NO<sub>3</sub>), lambda-cyhalothrin (C<sub>23</sub>H<sub>19</sub>ClF<sub>3</sub>NO<sub>3</sub>), imidacloprid (C<sub>9</sub>H<sub>10</sub>ClN<sub>5</sub>O<sub>2</sub>), tebuconazole (C<sub>16</sub>H<sub>22</sub>ClNO<sub>30</sub>), metalaxyl (C<sub>15</sub>H<sub>21</sub>NO<sub>4</sub>), mancozeb (with Zn and Mn additive), propineb (C<sub>5</sub>H<sub>8</sub>Cl<sub>2</sub>S<sub>4</sub>Zn), 1,2,4-D isooctylester (C<sub>8</sub>H<sub>6</sub>Cl<sub>2</sub>O<sub>3</sub>), cycloate (C<sub>11</sub>H<sub>21</sub>NOS), HCB (C<sub>6</sub>Cl<sub>6</sub>), α and β-HCH (C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub>), heptachlorine (C<sub>10</sub>H<sub>5</sub>Cl<sub>7</sub>), aldrin (C<sub>12</sub>H<sub>8</sub>Cl<sub>6</sub>), dieldrin (C<sub>12</sub>H<sub>8</sub>Cl<sub>6</sub>O), pp DDE (C<sub>14</sub>H<sub>10</sub>Cl<sub>4</sub>), pp DDD (C<sub>14</sub>H<sub>10</sub>Cl<sub>4</sub>), pp DDT (C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub>), op DDT (C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub>). Pesticide products, which are generally synthetic, turn into other chemical compounds in nature after chemical decomposition. An example is the change of Aldrin to Dieldrin in the decomposition of DDT by hydrolysis of chloride. The decomposition of the pesticide types is

**Fig. 6 a** Organic material (*OM*) vs.  $\text{NH}_3$  and **b** *OM* vs.  $\text{NH}_4$



very slow and the residues formed remain in the soil, air and water. When organic substances and clay contents increase, the pesticide content is reduced due to the adsorption and the absorption of the pesticides (Böhlke 2002).

Pesticides values in groundwater sampled from GW-5 and GW-19 were not suitable in terms of  $\beta$ -endosulphan with 0.2  $\mu\text{g}/\text{l}$  and in terms of 2, 4-D with 3.8  $\mu\text{g}/\text{l}$  according to the European Union Standards (EU, 1998 which accepts the limits 0.1  $\mu\text{g}/\text{l}$  for all types of pesticides), respectively. However, those values were not over according to EPA, 2003 that accept allowable limits 74  $\mu\text{g}/\text{l}$  for  $\beta$ -endosulphan and for 70  $\mu\text{g}/\text{l}$  2, 4-D. The newly used types of pesticides rapidly decomposed in the environment and leave a very small amount of residue, and they may account for this result. Moreover, the adsorption of the pesticides in clays and organic materials may also reduce these values below the detection limits. The high content of Zn in GW-3; GW-13, GW-14; GW-16 and GW-19 may be from the mancozeb and propineb types of pesticides.

#### Surface water

In the water samples collected from Porsuk River at sections SW-2 and SW-VIII (SW-4) in 2000, the  $\text{NO}_3^-/\text{NH}_4^+$  ratio is low (Table 5, Fig. 8). The decrease in  $\text{NO}_3^-/\text{NH}_4^+$  ratio in SW-VIII station indicates denitrification.

Besides the nitrogen compounds, other pollutant elements are present such as Fe and Al in the Eskisehir plain (Böhlke 2002). As an example, Fe and Al values are high in (SW-4). *P* values are high in oxidizing environments at  $\text{pH} = 7$  and it is low in basic conditions.

The high Fe and Mn content of the samples collected from surface water was not only the contribution of industrial wastes but also results from the activity of organic substances and bacteria in a reductive environment. The existing oxides of  $\text{Fe}^{2+}$  and manganese in the soil are transferred to the water through solutions. The decomposition of the alkaline feldspars in the area from tuffs and clay material may cause the increase of  $\text{Al}^{3+}$  in SW-1, SW-2, SW-4, SW-VI and SW-VIII of the surface water. In the Porsuk River, starting from the recharge



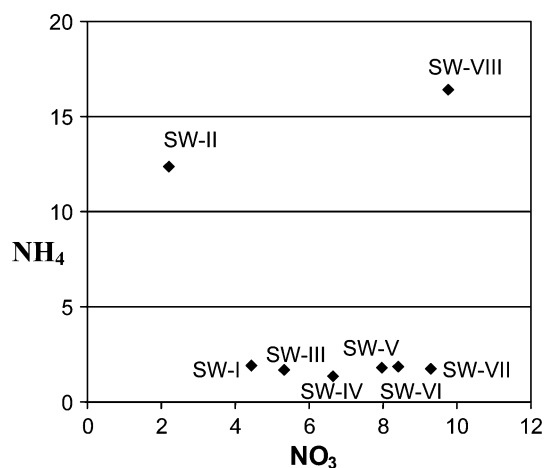


Fig. 8 NO<sub>3</sub> and NH<sub>4</sub> values (ppm) in Porsuk River, 2000

area, the outcropping ultramafic rocks may create a pollution of lithologic contribution of Fe, Mn and Al. The excessive Cr contents in some of the samples may also come from chromite deposits within the ultramafic rocks located in the catchment area (Cooper 2002).

In an anaerobic environment, the Fe/Mn ratio is high (Fetter 1999) in SW-1, SW-2, SW-4, SW-VI and SW-VII Porsuk River stations and in GW-3, GW-8 and GW-16 samples. The Fe/Mn ratio is low in GW-13, GW-9.2, GW-9.3 and GW-16. However, the Mn dissolves easier than Fe in the related Eh-pH range. In the transition zone, (anaerobic-aerobic) Fe/Mn ratio especially decreases with the sedimentation of Fe. Mn is adsorbed by clay material. Thus, the high Mn value is in conformity with the clay and organic substances contents in the area and after the underground discharge of the Sugar Factory wastes, the groundwater is affected and the Mn contents increase. The negative effects of the Sugar Factory are due to the wastewater from the washing of sugar beets. In general, K<sup>+</sup> and NH<sub>4</sub> are high and dissolved oxygen and NO<sub>3</sub> are low in such environments (Wersni et al. 2001). The samples collected from the wells in the area (GW-9.2 and GW-9.3) have high Mn, NH<sub>3</sub> and NH<sub>4</sub> contents but low NO<sub>3</sub> (Tables 1, 2). The high K<sup>+</sup> value in GW-9.2 may be due to the alcohol production unit in the Sugar Factory. Although the Mn, Fe and Al contents are low before the discharge of the Sugar Factory's wastewaters into the river, in the samples collected from the sampling location SW-III these contents become high in the samples from the SW-VI and SW-VII points. The high Cd in GW-19 is produced from mining fields and waste deposition areas. The high Pb in SW-3, GW-5, GW-6, GW-9.1 and GW-13 is from paints and batteries.

The municipal waste deposition site is located in the Takahasan valley, formed of carbonate rocks, near the

Eskisehir-Seyitgazi highway. The carbonate layers are semipermeable. The excessive pollution is due to the irregular deposition of the garbage. The leachate water from the waste deposition area is rich in heavy metals, organic substances, bacteria and salts that may chemically and biochemically decompose readily and infiltrate into the surface and groundwater, becoming one of the most important pollution sources. Leaching from the MWDA contained high levels of Pb, Cr, Mn, Cd, and Zn.

## Conclusions

The groundwater recharges to Porsuk River at both right and left banks until the Sugar Factory (around the samples GW-9.1, GW-9.2 and GW-9.3) area close to downtown. After this point, the Porsuk River begins recharging the groundwater at the left bank while groundwater continuous replenishing the Porsuk River at the right bank (Fig. 1). NH<sub>3</sub> in the Porsuk River has increased compared to previous years (SW-2 and SW-4). Oil and grease contents are also high in SW-1, SW-4, SW-III and SW-VIII. COD and BOD have increased. Especially samples of SW-VI, SW-VII and SW-VIII have become worse with the wastewater loadings from Sugar Factory and Organized Industrial Area. In the sample from SW-VIII section of the Porsuk River, phenolic material, free chlorine and sulfur values have increased. Porsuk dam reservoir is a hypolimnion lake and eutrophic condition exists there (anoxic environment). In the dry period, the water quality deteriorates compared to the wet period. Most of the groundwater samples are not suitable for drinking according to the both TDWS and EPA standards with respect to NO<sub>3</sub> and NO<sub>2</sub> values. The leaching of NO<sub>3</sub> from fertilizers and biocides during irrigation of agricultural land and leakage from overloaded sewage networks are sources of NO<sub>3</sub> pollution. NO<sub>3</sub> values are high in GW-7, GW-8, GW-19; NH<sub>3</sub> and NH<sub>4</sub> values are high in GW-1, GW-6, GW-8, GW-13, boron values are high in GW-1, GW-9.2 and NH<sub>4</sub>, SSM, NO<sub>2</sub>, S values are above the limits of drinking water standards. Phenol and NO<sub>2</sub> are high in GW-5. After the outlet of the water treatment plant, (DW-1), free chlorine, NO<sub>2</sub>, phenol, SSM, NH<sub>3</sub>, NH<sub>4</sub>, S, COD, organic nitrogen, oil and grease are higher than the allowable drinking water limits. The samples taken from GW-1, GW-9.2, and GW-16 are in Class III and IV with respect to boron values. GW-5 has high oil and grease content. In GW-7, DW-1, GW-3, GW-1, GW-9.2, sulfur and NH<sub>4</sub> are relatively high. Phosphorus is high in GW-1, GW-3, GW-5, GW-6, GW-7, GW-15, and GW-18 and phenol is very high in GW-3, GW-5, GW-8, GW-9.2, GW-13, GW-19, and DW-1. In respect to the heavy metal contents, ground-

water samples at GW-5 (Al), GW-6 (Cd), GW-8 (Fe), GW-9.2 (Mn), GW-9.3 (Mn), GW-13 (Cr and Mn), GW-15 (Mn), GW-16 (Fe and Mn), GW-19 (Cd) indicate heavy metal contaminations exceeding drinking water limits. GW-6, GW-13 and GW-16 are in Class III in terms of heavy metal contents. In surface water samples from Porsuk River, heavy metal contents increase towards downstream associated with the wastewater contamination from Sugar Factory and Organized Industrial Area. GW-19 is the spring under the influence of MWDA. In SW-7 sample, representing the leachate from MWDA, the high Pb, Cr, Mn, Cd, Zn and organic material contents result from the oxidation–reduction potential of the environment. Cd, Fe and B are also high in the soil samples taken from the downstream of the MWDA. This indicates the contamination sourced from the MWDA. In the Sugar Factory area, EC, S, organic substances, B, P<sub>2</sub>O<sub>5</sub>, Fe, Mn, Zn, and Pb are high. The increase in heavy metal contents downstream of Porsuk River is due to the industrial activities and discharge of their wastewater directly into the river. In groundwater samples of GW-1 (in dry period), GW-5, and GW-7 the anaerobic conditions may prevail. NO<sub>3</sub> values are over 10 mg/l in all samples except in GW-12 and DW-1 samples. The environments rich in Fe and Al are adsorbent for phosphorus where SW-I (SW-1) is an example with high Fe, Al and P<sub>2</sub>O<sub>5</sub> contents. Concerning pesticides pollution, no values are above the limits of EPA. However, two of the samples have pesticides concentrations above the EU limits for drinking water. In conclusion, N and P daughters (byproducts) and heavy metal contents are continuously increasing in the groundwater of the Eskisehir plain and in the Porsuk River according to the comparison of the recent and previous analyses results.

## Recommendations

The relation between Porsuk River and groundwater should be investigated in detail by gauging the surface waters in selected sections. Environmental isotopes should be used in the investigations, which will provide additional data to evaluate surface and groundwater interactions. The effect of the municipal waste deposition should be investigated in detail and precautions should be taken to rehabilitate the depositional conditions. Water treatment plant, municipal wastewater treatment plant, as well as Sugar Factory and the other treatment systems should be rehabilitated and direct discharge of wastewaters into the Porsuk River must be stopped. Biological treatment and modern techniques should be used to remove nitrogen and phosphorus from waste waters. A systematic sampling and analyzing program should cover the entire area and precautions should be taken against all kinds of pollution. It would be highly desirable if the entire recharge areas of the Porsuk River Basin is regarded as a special case when defining the best agronomic management and industrial practices, taking into account possible groundwater quality deterioration. The increasing demand for clean and potable water in the twenty-first century enjoins us to protect all our water resources.

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