Environ Earth Sci (2016) 75:170
DOI 10.1007/s12665-015-4986-2

ORIGINAL ARTICLE

Assessment of impact of environmental pollution on groundwater and surface water qualities in a heavily industrialized district of Kocaeli (Dilovası), Turkey

Irfan Yolcubal[1] · Özge Can Gündüz[1] · Fatmanur Sönmez[1]

Received: 13 July 2015 / Accepted: 30 September 2015 / Published online: 6 January 2016

Abstract The impact of uncontrolled industrialization and urbanization on surface water and groundwater qualities was assessed in a heavily industrialized district of Kocaeli (Turkey) considering source, types and levels of contaminants. A sampling campaign was conducted on both water bodies in dry (September) and wet (May) sampling periods. Water samples were taken from 6 surface water stations and 24 wells distributed from upstream to downstream along Dil stream to determine the degree of deterioration in water quality from background conditions. Results showed that Dil stream was heavily polluted with regard to many parameters including Al, Fe, Mn, Pb, DO, COD, NH_4, NO_2 and PO_4. While sewage discharges, leachates from closed wild landfill and quarries create sources of contamination for Dil stream at upstream, primarily metal industries (mainly iron and steel manufacturing) at downstream contribute markedly to the metal contamination. Contribution of highly polluted Dil stream to the groundwater contamination is also significant in the alluvium aquifer at both upstream and downstream of Dil stream. Microbial pollution indicating fecal contamination and high nutrient levels exist in the groundwater. In addition, relatively high AOX concentrations over background levels were detected in wells at the downstream part of Dil stream where industrial activities were densely distributed. Deep wells located near the Gulf of İzmit were also affected by seawater intrusion. Results suggest that Dil stream contaminated by industrial discharges, sewages, and leachates from old wild landfill negatively influences the groundwater quality in the alluvial aquifer.

Keywords Groundwater contamination · AOX · Heavy metals · Surface water

Introduction

Rapid and irregular industrialization and urbanization in Turkey cause environmental pollution threatening public and environmental health seriously. Dilovası district of Kocaeli in the Marmara Region (Fig. 1) with 45,000 inhabitants is a symbol of Turkey's uncontrolled industrialization and is located at the center of a highly industrialized area.

Industrial and residential settlements in the region cover 40 and 25 % of Dilovası surface area, respectively. In the Dilovası organized industrial zone, there are 193 companies serving in 45 different sectors including mainly metal (iron–steel, aluminum and smelting) and chemical (e.g., paint, detergent) industries and quarries. Two of the busiest highways (O4 and D-100) of Turkey pass through the heart of Dilovası. As a result of both heavy traffic and industrial activities near residential areas, air (Ergenekon et al. 2009; Dogruparmak and Ozbay 2011; Demiray et al. 2012; Kuzu et al. 2013; Pekey and Ozaslan 2012; Ozturk et al. 2015) and soil (Yaylalı-Abanuz 2011; Cetin 2014) pollutions are among the major environmental problems in the region. For instance, a recent biomonitoring study conducted in Dilovası by our research laboratory (Demiray et al. 2012) revealed that mean metal (Mn, Pb, Cd, Zn, Fe, Ni, Cu, Al, Hg, As and V) concentrations of lichen samples in Dilovası were two to sevenfolds higher than those in the urban districts of Kocaeli. Demiray et al. (2012) also pointed out that metal industry (iron–steel, aluminum and zinc), fossil fuel combustion and heavy traffic contributed significantly to the metal emission in Dilovası region.

✉ Irfan Yolcubal
yolcubal@kocaeli.edu.tr

[1] Department of Geological Engineering, University of Kocaeli, Umuttepe Kampüsü, 41380 Kocaeli, Turkey

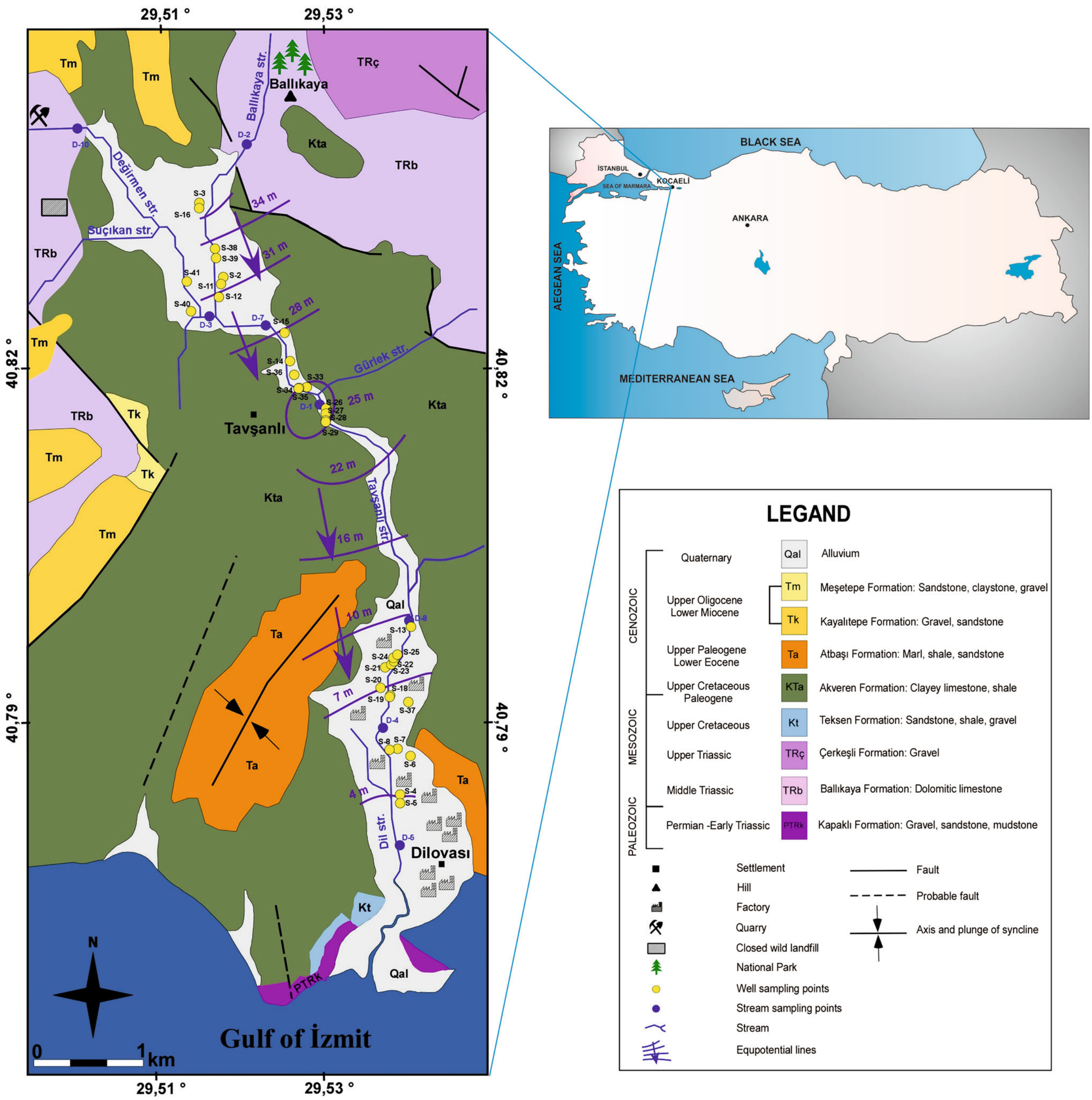

Fig. 1 Hydrogeology map of study area. Groundwater and surface water sampling points are also shown on the map

The impact of pollution on human health in Dilovası was also reported in several studies. Hamzaoglu et al. (2014) reported that mean heavy metal concentrations of Al, As, Cd, Cu, Fe, Hg, Pb and Zn in colostrum (breast milk) and meconium (baby faeces) were all higher in samples from the industrial district (Dilovası) than the non-industrial district. They also showed that As, Cd, Cu, Fe Hg, Pb and Zn concentrations in the breast milk from pregnant women were higher than the limit defined by the World Health Organization (WHO). In Dilovası region, the proportion of deaths caused by cancer is three times higher than both the national and world data records (Hamzaoglu et al. 2011). Environmental pollution problems in Dilovası also came to the attention of the Grand National Assembly of Turkey and a report was prepared describing preventive actions to be taken (TBMM 2006).

In the region, industries are generally populated along the downstream of Dil stream, which discharges into the Gulf of İzmit (Fig. 1). Residential areas, quarries and a closed wild landfill are also located in the drainage network of the Dil stream (Fig. 1). Inefficient operation of wastewater treatment plants by factories, domestic wastewater discharges from residential areas and leachates from landfill create serious surface-water pollution for both Dil stream and the Gulf of İzmit. In addition, the surface water pollution in Dil stream also threatens the groundwater quality in the alluvial aquifer extending along Dil streambed. Although there are numerous studies about the air pollution problem in Dilovası, the impact of uncontrolled industrialization on both surface and groundwater qualities in the region was not thoroughly investigated. A single work conducted by Bingöl et al. (2013) partially presented the degree of heavy metal pollution in Dil stream and the Gulf of İzmit.

The deterioration in the surface and groundwater qualities in the industrialized regions is a widespread problem around the world and reported in relevant studies (Sponza and Karaoğlu 2002; Naik et al. 2007; Krishna and Mohan 2014; Kara et al. 2015). The main objectives of this study were to assess the impact of industrialization and irregular urbanization on both groundwater and surface water (Dil stream) qualities in Dilovası region to determine potential pollutant sources and linkage between Dil stream and groundwater in the alluvial aquifer with respect to water quality.

Hydrology and hydrogeology of site

Dilovası is placed on a bowl-like plateau surrounded by low hills along Dil stream. The northern part of the site is bordered by the Gulf of İzmit (Fig. 1). Dil stream (also called Tavşanlı stream) is the main surface water body in the study area (Fig. 1). At the upstream of Dil stream near the village of Tavşanlı, Ballıkayalar Valley Natural Park is located. The park with an area of 1603 ha has been under protection by Turkish Ministry of Forestry and Water Affairs since 1991. Stream flow in Dil stream is from northwest to south direction and discharges into the Gulf of İzmit in Dilovası. It is 12 km long and has a drainage area of 129 km^2. Monthly average discharge rate of the stream is 1.06 m^3/s (±0.88). The highest discharge rate occurs in December with an average of 2.78 m^3/sn while the lowest rate of discharge takes place from June to September (0.12–0.2 m^3/s). Annual average discharge volume of the stream is around 34 million m^3. Dilovası has a marine climate with a mean annual rainfall of 751 mm.

Alluvium exposed along the Dil stream is the main aquifer system and is composed of sandy gravel, sand and clay (Fig. 1). Their surface area is around 5 km^2 and is about 8 km long and 0.1–1.2 km wide. The thickness of the alluvium ranged 15–35 m from south to north. Coarse-grained units in alluvium are generally located at the depths of 7–10 m and 25–30 m. Alluvium is underlain by Campanian-Early Eocene aged Akveren formation that is composed of clayey limestone. This unit, which shows a wide areal distribution in the study area, demonstrates generally impermeable character. However, the fractured sections of the unit can hold groundwater. Groundwater flow direction in the alluvial aquifer is towards the Gulf of İzmit (Fig. 1). There are many wells drilled in the alluvial aquifer to supply water demands of the industries in Dilovası. Wells are found at both upstream near Tavşanlı and downstream locations in Dilovası where the industrial settlements are densely distributed. The depth of dug wells in the alluvium ranged from 5 to 20 m and uniformly distributed along Dil stream. The depth of deep wells screened in both alluvium and clayey limestone reaches up to 254 m (40–254 m). The alluvial aquifer is recharged from mainly surface runoff. For the investigated wells only, annual groundwater pumping from alluvial aquifer by industry equals to 76 % of the safe yield of the aquifer. Therefore, industry in the region poses great pressure not only on groundwater quality but also on quantity.

Methods

A sampling campaign was conducted on both surface water (Dil stream) and groundwater in the alluvial aquifer in May and September of 2011 to assess the impact of industrial activities on their water qualities. Out of 34 wells, 24 wells located along Dil stream were monitored for assessing groundwater quality. In addition, stream water quality was monitored at six sampling stations along the Dil stream (Fig. 1). Groundwater and surface water sampling points were selected from both upstream and downstream locations of Dil stream to determine the degree of deterioration in water quality from background conditions.

For determining major and trace element contents of groundwater, water samples were filtered with 45 μm cellulose acetate syringe filter and then acidified to pH < 2 with suprapur nitric acid in situ. The total (dissolved + suspended) element concentration of surface water was measured after digested following EPA 3015A method (2007). Elemental analyses on water samples were conducted with Inductively Coupled Mass Spectrometer (ICP-MS, Perkin Elmer DRC-e). Analytes were selected mainly based on the potential pollutant sources in Dilovası as well as listed parameters in current national and international quality standards and guidelines defined for surface waters and groundwater.

Filtered and unacidified water samples were also collected for measuring anion (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, F^-, PO_4^{3-}) concentration and total alkalinity. Anion and alkalinity measurements were conducted with ion-chromatography (Dionex IC-1100) and titration methods, respectively. The pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature (T) measurements of the samples were performed in situ (Thermo Orion Five Star). Turbidity of samples was measured with Hach 2100 N Turbidity meter. NH_4 content of the samples was quantified with Hach DR 500 Spectrometers (ISU Labs.). Chemical oxygen demand (COD) of surface water samples was also measured to determine the amount of organic pollutants found in surface water. COD of the samples was measured with Open Reflux Method (SM-5220B) (APHA 2012).

To investigate the influence of domestic sewage discharge to Dil stream on groundwater quality, sterile groundwater samples were also taken from wells in 250 mL sterile polyethylene bottle for determining microbial constituents (Coliform Bacteria, *E. coli*, *Enterococci*, Max Colony number at 37 °C, 48 h) with membrane filtration method (ISU Labs.). Prior to the collection of samples, the sampling port was sterilized using isopropyl alcohol.

To determine the level of potential halo-organic groundwater contaminants, adsorbable organic halides (AOX) sampling was also conducted in selected wells (i.e., 19 wells) located at both upstream and downstream parts of Dil stream. Filtered water samples were adjusted to a pH < 2 with nitric acid in situ, sealed in 1 L amber bottle and maintained at 4 °C until analysis (AOX analyzer, TUBİTAK MAM Labs). Detection limit of AOX is 3.5 µg/L.

Correlation and cluster analyses were also conducted on the heavy metal contents of surface water (Dil stream) to evaluate the relationship between the pollutants and common pollutant sources. Correlations between elements were tested by the Pearson's correlation test ($P < 0.01$, 0.05). Two-tailed significance values were used for the correlation test. Cluster analyses were performed using the SPSS v.20 program package. Complete linkage clustering method and squared Euclidean distance metric were used in the cluster analysis. To compensate different magnitudes in metal concentrations of surface water samples, each variable was standardized by subtracting its sample mean and then dividing by its sample standard deviation (z-score) before doing the clustering (Demiray et al. 2012).

Results and discussion

Surface water quality

To determine the impact of uncontrolled industrialization and urbanization on water quality, surface water sampling was conducted along Dil stream from upstream (Ballıkayalar) to the Gulf of İzmit (Fig. 1). Sampling was conducted in May and September to monitor seasonal variation in water quality. Water samples obtained from upstream (e.g., D2 in Fig. 1) where Ballıkayalar National Park is located represents the baseline conditions (uncontaminated part) for the Dil stream. Results are presented in Tables 1 and 2.

Dil stream at upstream shows alkaline pH (8.36–8.71) and moderate EC (555–566 µS/cm) values. Total alkalinity of stream ranges between 180 and 263 mg/L $CaCO_3$. Stream shows Ca-Mg-HCO_3 water type. At the upstream of Dil stream, Dolomitic limestone (Ballıkayalar Formation) is cropped out (Fig. 1). Physico-chemical characteristic of upstream is coherent with local geology.

From upstream to downstream, where wastewater discharges from residential areas and industries occur, the water type of Dil stream changed from Ca-Mg-HCO_3 to Na-Ca-Cl-HCO_3 and Na-Ca-Cl-HCO_3-SO_4. The pH of the stream also showed one unit drop while EC exhibited an increase along flow direction (Fig. 2a, d). The increase in EC value of stream was mainly controlled by an increase in Na concentration (Fig. 2d).

Drop in DO concentration or increase in COD of stream was also distinct along the flow path. With the contribution of drainages from Tavşanlı region (D3, Fig. 2b, c), dissolved oxygen content of stream decreased from 6.5–6.8 to 0.3–2 mg/L. Similarly, COD content of stream showed almost 13- to 25-fold increase from <15–33 to 387–438 mg/L. Nutrient contents of stream also exhibited significant increase. This was especially distinctive in NH_4^+, NO_2^- and PO_4^{3-} contents (Fig. 2e, f). Despite seasonal variation, ammonium and nitrite concentration of stream at Tavşanlı intersection (D3, Fig. 2e, f) was about 13–38 and 30.6 mg/L, respectively. Deterioration in water quality of Dil stream was especially evident in dry period (Sept. 2011), when the low flow conditions under the control of wastewater discharges exist (Fig. 2) and continued to downstream from Tavşanlı region. At the west of Tavşanlı intersection where flows coming from Değirmen and Suçıkan streams meet, a closed wild landfill is located on drainage area of Suçıkan stream (Fig. 1). Leachates from this area in rainy season create contamination for surface and groundwater bodies at the downgradient locations. The decrease in DO and increase in COD and nutrient concentrations at the Tavşanlı intersection of Dil stream indicated sewage discharge from Tavşanlı residential areas and leachates from old wild landfill as potential sources.

Metal contents of the Dil stream also showed dramatic change from upstream to downstream. At the upstream (e.g., Ballıkayalar), the background metal concentrations of Dil stream were in the limits of clean (unpolluted) surface water quality (Class I, Table 2). However, at the downstream, the quality of Dil stream significantly

Table 1 Physicochemical characteristics and major ion contents of Dil stream at different sampling locations along flow path in dry (September 2011) and wet (May 2011) sampling period

Sampling period	Sample no	pH	DO (mg/L)	EC (µS/cm)	Total alkalinity (mg/l $CaCO_3$)	Turbidity (NTU)	COD (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	PO_4^{3-} (mg/L)
May 2011 (wet season)	D2	8.36	6.8	555	263	0.86	<15	17	3	18	86	0	19	21	317	4.4	<0.1	<0.5
	D3	7.81	2.1	1212	447	163	387	88	15	17	110	13	107	71	546	1.9	30.6	4.0
	D1	7.85	4.7	1044	347	0.22	132	84	18	18	109	0	90	77	424	50.6	<0.1	2.5
	D4	7.51	1.9	1180	399	45	280	105	14	17	116	0	100	117	487	7.2	42.8	<0.5
	D5	7.46	3.3	1890	243	27	134	190	16	25	129	12	299	163	296	<0.1	<0.1	<0.5
September 2011 (dry season)	D2	8.71	6.5	566	180	1	33	30	4	18	64	0	43	31	218	1.7	<0.1	<0.5
	D10	8.13	6.63	882	78.8	150	42	71	14	19	81	3	113	154	96	15.2	1.1	<0.5
	D3	8.14	0.3	1660	305	77	438	170	18	18	104	38	216	156	371	<0.1	<0.1	<0.5
	D7	8.30	0.8	2053	333	162	757	207	31	23	109	70	309	181	405	<0.1	<0.1	2.55
	D1	7.66	0.4	1732	331	1	462	180	20	18	100	42	234	159	404	<0.1	1.22	<0.5
	D8	7.96	0.1	1579	358	3236	610	167	26	20	85	0	184	142	430	2.4	1.08	<0.5
	D4	8.03	0.4	2227	440	94	623	273	27	16	65	0	245	242	535	<0.1	<0.1	<0.5
	D5	7.66	0.1	2090	365	111	445	239	25	19	105	45	257	282	440	<0.1	1.35	<0.5
Turkish environmental guidelines for inland waters																		
Class I		6.5–8.5	8	–	–	–	25	125	–	–	–	0.26	25	200	–	22	0.007	0.06
Class II		6.5–8.5	6	–	–	–	50	125	–	–	–	1.3	200	200	–	44	0.03	0.5
Class III		6.0–9.0	3	–	–	–	70	250	–	–	–	2.6	400	400	–	88	0.16	2
Class IV		<6–9<	>3	–	–	–	>70	>250	–	–	–	>2.6	>400	>400	–	>88	>0.16	>2

Samples were ordered from upstream to downstream

Table 2 Metal contents of Dil stream at different sampling locations along flow path in dry (September 2011) and wet (May 2011) sampling period

Sampling period	Sample no	Al (mg/L)	Fe (mg/L)	Mn (mg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Cr (µg/L)	Co (µg/L)	Cu (µg/L)	Hg (µg/L)	Pb (µg/L)	Sb (µg/L)	V (µg/L)	Zn (µg/L)
May 2011 (wet season)	D2	0.04	0.05	0.02	1.7	46	68	0.01	<0.01	0.3	0.5	<0.01	0.06	0.07	1.7	<0.01
	D3	13.6	8.1	0.7	5.3	95	156	0.15	21.3	2.6	16.2	0.39	44.0	0.8	5.7	290
	D1	8.6	7.7	0.5	6.1	92	165	0.14	3.3	2.1	9.4	0.11	40.1	0.7	5.3	72
	D4	14.5	9.1	0.4	5.5	123	155	0.13	20.3	2.8	10.6	0.18	40.4	0.8	7.3	79
	D5	2.9	1.6	0.06	3.6	303	119	0.14	3.6	1.3	5.8	0.04	7.3	0.7	4.4	85
September 2011 (dry season)	D2	0.01	<0.0001	0.004	1.7	44	60	<0.01	<0.01	0.1	0.8	0.01	0.07	0.1	1.7	<0.01
	D10	14.7	5.8	0.03	4.0	190	83	0.04	1.6	5.6	4.6	0.03	2.2	0.6	12.3	28
	D3	14.7	11.0	1.0	6.0	152	115	0.06	5.3	3.8	9.5	0.21	13.3	1.1	9.2	39
	D7	16.3	21.6	1.1	7.7	96	123	0.06	26.1	5.1	8.4	0.42	32.4	0.8	7.3	30
	D1	11.3	11.4	1.0	5.8	123	128	0.05	1.6	3.9	7.4	0.30	13.7	0.9	5.7	45
	D8	101	57.7	1.5	4.3	51	339	0.02	9.5	5.4	8.5	0.35	40.6	0.1	10.9	30
	D4	8.6	3.1	0.3	4.4	437	81	0.08	3.3	2.5	18.9	0.41	5.3	1.7	7.8	59
	D5	25.7	14.6	0.6	5.7	297	133	0.21	7.1	4.1	10.5	0.63	24.8	0.9	14.3	104
Turkish environmental guidelines for inland waters																
Class I		0.3	0.3	0.1	20	1000	1000	3	20	10	20	0.1	10	–	–	200
Class II		0.3	1	0.5	50	1000	2000	5	50	20	50	0.5	20	–	–	500
Class III		1	5	3	100	1000	2000	10	200	200	200	2	50	–	–	2000
Class IV		>1	>5	>3	>100	>1000	>2000	>10	>200	>200	>200	>2	>50	–	–	>2000

Samples were ordered from upstream to downstream

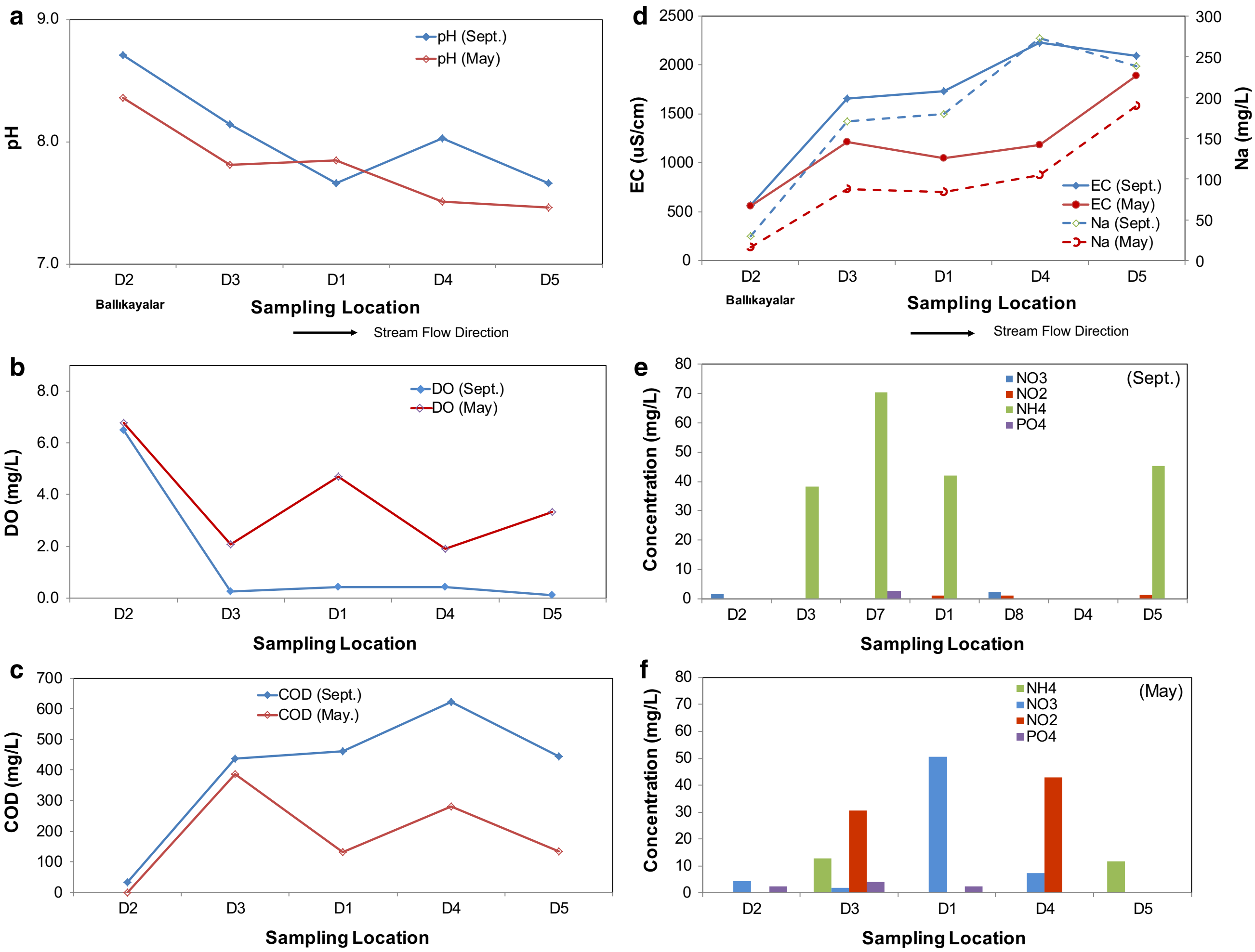

Fig. 2 Change in **a** pH, **b** DO, **c** COD, **d** EC and Na and **e**, **f** nutrient contents of Dil stream along flow path at dry (September 2011) and wet (May 2011) periods

deteriorated with the contribution from Değirmen stream at the Tavşanlı region (D3) and momentary discharges from iron–steel factory at the downstream (D8) (Figs. 1, 3). This was evident especially in Al, Fe and Mn contents of Dil stream. Al content of Dil stream showed an abrupt increase at Tavşanlı intersection from 0.01 to 14 and 100 mg/L near the iron–steel factory (D8) (Fig. 3a, b). Mn and Fe also showed similar concentration profile (Fig. 3a, b). This was observed in both wet and dry season samplings. These metals exhibited relatively high concentrations in dry season sampling due to low flow conditions of the Dil stream. Analysis of water sample (D10) obtained from Değirmen stream, which drains from rock quarry, showed high Al (14.7 mg/L) and Fe (5.8 mg/L) concentrations similar to the water samples at the Tavşanlı intersection (D3) at the dry sampling period (Table 2). These samples (D3 and D10) also exhibited high turbidity values (150–162 NTU) (Table 1; Fig. 4a). These results showed that rock quarries at Tavşanlı region was one of the point sources causing metal contamination in Dil stream.

Another point source for these metals was found at the downstream of Dil stream (D8). Red coloring of Dil stream near iron–steel factory was clear evidence of the source (Fig. 4b). Al (101 mg/L), Fe (57.7 mg/L) and Mn (1.5 mg/L) contents of the stream near factory also showed significant increase relative to those of upstream sampling locations (Fig. 3a). These results indicated that Dil stream was severely contaminated with respect to Fe, Al and Mn.

Low values observed at the down gradient location (D4 and D5) from factory (D8) in dry sampling period (September) represented the pre-discharge conditions in Dil stream. D8 sampling point was not in the actual sampling program. During wet (May 2011) sampling period, a momentary discharge to the stream (Fig. 4b) was noticed with its distinct color and flow then added to the sampling program.

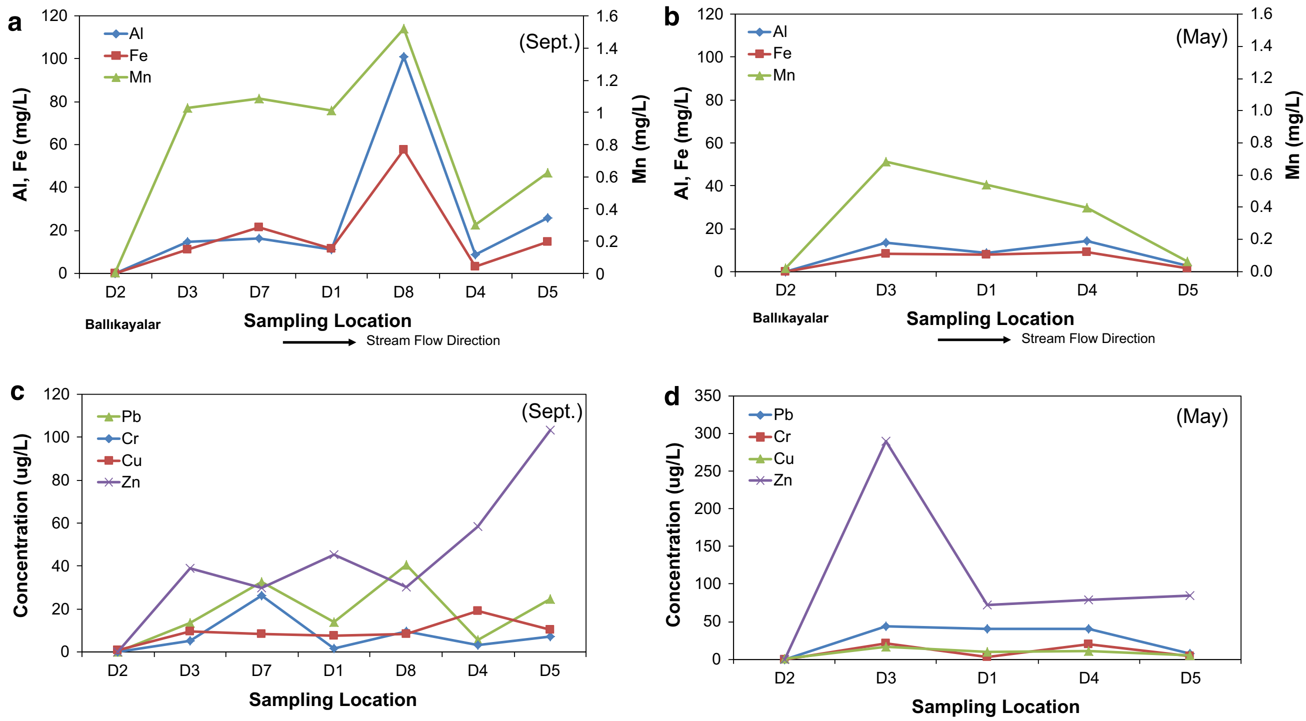

Fig. 3 Change in metal contents of Dil stream along flow path at dry (September 2011) and wet (May 2011) periods. Metals showing significant anomaly were only plotted

Fig. 4 A view from **a** D3 and **b** D8 surface water sampling points along Dil stream. Note turbidity and coloring in stream resulting from Değirmen stream at Dil stream intersection (D3) and near iron–steel factory (D8), respectively

Deterioration in water quality was also evident in the Pb, Cr, Cu and Zn contents of Dil stream (Fig. 3c, d). Although there was a noteworthy deviation from baseline conditions along the flow path with respect to these metals, this was not as severe as Fe, Al and Mn. All these results suggest that metal industry in the Dilovası region contributes markedly to the metal contamination in Dil stream.

To verify the common pollutant sources for high metal concentrations in Dil stream, cluster and correlation analyses were performed on surface water metal data. The results are presented in Fig. 5. Classification of metals revealed two main clusters: cluster 1 consisted of single group (Al–Fe–Mn) and cluster 2 subdivided into two subgroups (2a: Pb–Cr, 2b: Cu–Zn). Correlation analysis showed that Fe is strongly correlated with Al ($r = 0.967$, $P < 0.01$) and Mn ($r = 0.698$, $P < 0.01$). These elements (cluster 1) also had a linkage with Pb–Cr ($r = 0,672$, $P < 0.05$) and Cu–Zn ($r = 0.53$) (Fig. 5). These results suggest that cluster 1 elements come from a common source. Cluster 1 and 2 metals were listed among many other iron and steel toxicants in direct discharges (EPA 2002), indicating iron and steel manufacturing in Dilovası is one of the significant point sources for these metals. Strong correlation between Al and Fe, which are the most abundant elements in earth crust points out quarries on the upstream of Dilstream as another potential source for these metals in Dil stream. Clustering of Cu–Zn and Pb–Cr

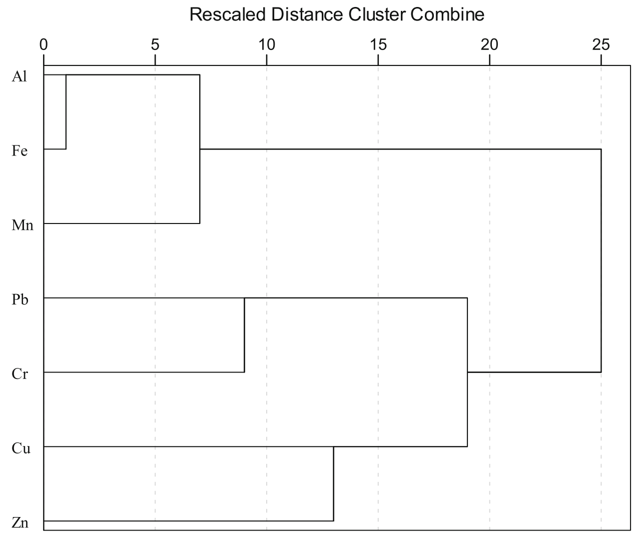

Fig. 5 Dendrogram of selected metals in Dil stream samples

suggests smelting, refining and plating of nonferrous metals for possible source.

Water quality regulations in Turkey classify inland waters into four classes. Classes I and II refer to clean–fairly clean waters suitable for domestic usage after treatment, irrigation and recreational purposes. Class III refers to polluted water suitable for industrial water after treatment. Class IV includes heavily polluted water that is not suitable for any purpose at all. According to Turkish surface water criteria, Dil stream water quality is classified as class III for Mn and Pb, class IV for Al, Fe, DO, COD, NH_4^+, NO_2^-, PO_4^{-3} and classes I–II for the rest of the investigated parameters (Tables 1, 2).

Groundwater quality

To evaluate the impact of surface water pollution on groundwater quality, groundwater sampling was also conducted accordingly at the upgradient and downgradient locations of alluvial aquifer along Dil stream (Fig. 1).

Groundwater in alluvial aquifer generally exhibits neutral pH values. Alkaline pH values were measured in deep wells screened in clayey limestone unit. Seasonal variation in pH values was observed in alluvial aquifer. In September sampling period, while 36 % of the wells exhibited pH values greater 7, this ratio rose up to 60 % in May sampling period (Tables 3, 4). In the later period, the increase observed in pH values of shallow wells points out the recharge from Dil stream.

Electrical conductivity of groundwater displays a relatively wide range values (578–2717 µS/cm, average 1134 ± 512 µS/cm) (Tables 3, 4). Depending upon sampling period, 48–60 % of the wells exhibit EC values over 1000 µS/cm. In most wells, EC values measured in the dry sampling period showed an increase with respect to those of wet period. High EC values were observed in wells (S-4: 2241–2460 µS/cm; S-5: 2453–2717 µS/cm; S-8: 2209–2254 µS/cm) located at the downstream part of Dil stream (Tables 3, 4). As compared to the others, these wells are located near Gulf of İzmit at 6–14 m amsl. Well depth of S-4, S-5 and S-8 is 72, 75, and 194 m, respectively.

Mean dissolved oxygen (DO) concentration of groundwater in Dilovası was around 3.5 ± 1.7 mg/L. 18–2 % of the wells exhibits DO values above 5 mg/L. Wells having low DO values (<2 mg/L) were S-2, S-12 and S-23 dug wells and S-4, S-36 and S-40 deep wells (Tables 3, 4). These wells were distributed at both upstream and downstream of Dil stream (Fig. 1).

Although different hydrochemical water facies were observed in groundwater in Dilovası, Ca-Mg-HCO_3 water type was the dominant water facies. In dry (September) sampling period, while groundwater was over saturated with respect to calcite, aragonite and dolomite in 96, 80 and 48 % of the wells, respectively, these percentages dropped to 44, 25 and 23 % in wet (May) sampling period for the respective minerals. High Ca contents of groundwater result from carbonate rock–water interaction in the recharge area of aquifer.

Variation in water facies of groundwater (Fig. 6) points out mixing of different water bodies in Dilovası. Change in dominant cation and anion types from Ca–Mg to Na and HCO_3 to Cl, respectively, indicates mixing of water enriched with Na and Cl with groundwater (Fig. 6). Dil stream and seawater intrusion in some wells had an influence in such mixing. Cl (504 ± 102 mg/L) concentrations measured in wells (S-4, S-5 and S-8) near the Gulf of İzmit were almost two times higher than those of Dil stream (225 ± 87 mg/L) at the downstream. Water facies (Na-Cl-HCO_3, Na-Ca-Mg-Cl-HCO_3, Ca-Mg-Na-Cl-HCO_3) observed in these wells point out a mixing of groundwater with seawater at some proportion.

To see the impact of Dil stream and seawater on the groundwater quality better, Cl/HCO_3 ratios of water samples plotted on Cl vs Cl/HCO_3 graph. As seen in Fig. 7, there was a significant correlation between Cl vs Cl/HCO_3 with *r*-squared values of 0.82 and 0.98. While Dil stream background samples (Ballıkayalar) were placed close to origin, polluted stream samples were located at the upper parts on the line (Fig. 7a). Wells were mostly placed inbetween these two limit values, except for S-4, S-5 and S-8. These later wells exhibited higher Cl and Cl/HCO_3 ratios and were placed at the outside of upper limiting values on the line. These results suggest that deep wells (S-4, S-5 and S-8) near Gulf of İzmit were influenced by seawater intrusion to the some extent.

Table 3 Physicochemical characteristics and major ion contents of well samples in wet (May 2011) sampling period

Well no	Location/ well depth (m)	*T* (°C)	pH	DO (mg/L)	EC (µS/cm)	Total alkalinity (mg/l $CaCO_3$)	Turbidity	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	PO_4^{3-} (mg/L)	F^- (mg/L)
S-2	Basf (15)	13.4	7.48	2.23	607	120	0.26	12	1.6	12.7	29.1	0	18.8	24.1	145.2	5.3	<0.1	<0.5	0.3
S-4	Olmuksa (72)	18.2	7.16	0.79	2241	384	4.35	266.4	13.0	38.3	72.5	15.2	435.3	23.7	465.9	35.4	<0.1	2.5	0.4
S-5	Olmuksa (75)	18.4	6.94	3.43	2453	269	5.42	167	2.7	80.3	140.0	0.5	579.8	42.1	326	19.4	<0.1	<0.5	0.3
S-6	Izocam (196)	17.5	6.77	5.23	1136	216	0.36	25.6	1.1	28.0	79.3	0.1	88.9	59.1	263.7	64.7	<0.1	<0.5	0.3
S-7	Izocam (254)	18.2	6.96	3.08	1096	113	0.21	41.4	4.9	13.9	46.2	0.2	58.7	74	136	27.5	1.3	<0.5	0.3
S-8	Izocam (194)	18.5	6.93	3.79	2209	286	0.35	131	2.5	75.2	122.0	0.3	502.5	53.5	348.4	22.7	<0.1	<0.5	0.3
S-11	Diler Demir Demir (15)	14.1	7.22	4.53	704	133	0.38	21.1	2.6	13.8	42.5	0.6	29.1	31.8	160.1	5.3	<0.1	<0.5	0.3
S-12	Diler Demir Çelik (15)	13.7	7.24	2.16	1434	156	0.78	52.4	1.0	14.7	107.0	0.4	168.1	65.6	189.9	77.6	<0.1	<0.5	0.3
S-14	Diler Demir Çelik (15)	14.9	6.97	2.92	880	204	0.26	32.2	1.4	6.9	64.5	0.8	51.4	36.5	248.9	7.4	<0.1	<0.5	0.3
S-15	Diler Demir Çelik (15)	14.9	7.18	4.36	719	115	0.27	20.8	2.1	15.6	43.3	0.4	27.7	30.8	138.9	5.8	<0.1	<0.5	0.3
S-21	Çolakoğlu Metalurji (20)	15.7	7.26	2.99	1228	324	1.04	59.3	3.4	14.7	70.7	1.6	29.3	20.7	395.1	11.7	<0.1	<0.5	0.2
S-22	Çolakoğlu Metalurji (18)	16	6.85	3.17	1183	100	0.30	33.7	2.4	11.0	96.9	0.2	103.7	83.8	121.7	31.2	1.1	<0.5	0.3
S-23	Çolakoğlu Metalurji (20)	15.9	7.25	1.15	1137	138	0.27	31.1	2.4	9.8	117.0	0.1	118.7	59.6	167.6	26.1	<0.1	<0.5	0.3
S-24	Çolakoğlu Metalurji (6)	16.5	7.05	2.49	1036	88	0.19	23.7	2.1	9.0	79.4	0.1	93.1	46.4	106.4	29.2	<0.1	<0.5	0.3
S-25	Çolakoğlu Metalurji (20)	16.2	7.13	2.21	1066	125	0.30	28.6	2.9	10.7	101.3	0.1	102.6	46.5	152.3	29	<0.1	<0.5	0.3
S-26	Çolakoğlu Metalurji (30)	15	7.04	4.62	682	168	0.53	13.1	1.9	6.0	69.3	0.2	16.9	16.7	204.1	12.4	<0.1	<0.5	0.3
S-27	Çolakoğlu Metalurji (–)	14	7.4	5.85	774	119	0.30	24.8	2.5	10.2	52.6	0.2	34.3	26.4	145	12.4	<0.1	<0.5	0.3

Table 3 continued

Well no	Location/well depth (m)	*T* (°C)	pH	DO (mg/L)	EC (µS/cm)	Total alkalinity (mg/l $CaCO_3$)	Turbidity	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	PO_4^{3-} (mg/L)	F^- (mg/L)
S-33	Polisan (15)	13.9	6.86	6.45	616	120	0.57	4.4	0.9	4.3	41.4	0.3	8.4	12.5	146	12.9	<0.1	<0.5	0.3
S-36	Polisan (160)	13.7	6.86	1.82	905	108	0.46	31.7	2.8	9.6	46.1	1.4	40.5	25.1	130.4	28.4	3.4	<0.5	0.3
S-37	Dilmak Tanker (65)	15.2	6.71	5.45	1149	174	1.16	18.8	1.7	7.4	107.0	0	53.1	99.6	211.7	74.7	1.1	<0.5	0.3
S-38	Necati Tekin (200)	19.3	6.82	2.87	763	281	0.46	11.4	1.1	27.0	59.1	0	15.2	19.8	342.7	8.3	<0.1	<0.5	0.3
S-39	Necati Tekin (5)	17.1	7.35	2.61	609	188	0.18	12.9	2.4	14.4	57.2	0	20.5	22.5	228.2	5.3	<0.1	<0.5	0.3
S-40	Elgin Su (180)	15.2	7.99	1.65	820	324	7.65	131	2.1	9.6	44.0	0.7	46.6	56	391.8	2.5	2.1	<0.5	0.8
S-41	Kastamonu Entegre (180)	20.7	6.59	2.96	867	165	0.96	11.2	0.7	31.6	33.2	0	22.5	30.5	199.6	20.4	<0.1	<0.5	0.3
TSE 266 (2005)			6.5–9.5	–	2500	–	1	200	–	–	–	0.5	250	250	–	50	0.5	–	1.5
EPA (2009)			6.5–8.5	–	–	–	1	–	–	–	–	–	250	250	–	45	–	–	2

Table 4 Physicochemical characteristics and major ion contents of well samples in dry (September 2011) sampling period

Well no	T (°C)	pH	DO (mg/L)	EC (µS/cm)	Total alkalinity (mg/l $CaCO_3$)	Turbidity (NTU)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	PO_4^{3-} (mg/L)	F^- (mg/L)
S-2	18.2	7.11	1.7	674	185	0.70	21	2.9	13.7	85	0	28.1	26.5	225	2.9	<0.1	<0.5	0.3
S-4	16.9	7.09	0.93	2460	350	43.2	155	4.7	69.8	188	2.2	364.4	17.1	427	3.1	<0.1	<0.5	0.3
S-5	18	6.85	3.51	2717	273	0.45	195	3	79.2	192	0.3	650.7	46.5	333	17.9	1.1	<0.5	0.3
S-6	17.2	6.92	5.79	1173	315	0.40	28.8	1.2	29.6	163	0.1	105.3	54.1	385	60.1	<0.1	<0.5	0.3
S-7	17.7	7.04	4.7	1253	383	0.21	58.9	4.5	32.7	164	0.1	130.1	52.1	467	12.3	<0.1	<0.5	0.3
S-8	18.2	6.75	3.51	2254	275	0.30	128	2.4	73.5	191	0	493.6	48.2	336	18.5	<0.1	<0.5	0.3
S-11	18.5	6.96	2.63	883	310	0.31	37.4	2.9	16.3	85.7	0.1	53.1	46.4	378	3	<0.1	<0.5	0.3
S-12	15.4	6.71	1.87	1281	355	0.23	42.2	0.8	13.5	190	0.1	120.3	57.2	434	42.7	<0.1	<0.5	0.3
S-14	17.3	6.85	4.39	923	350	0.20	35.4	2.4	11.6	130	0.1	56.3	40.3	428	6.3	1.1	<0.5	0.4
S-15	16	6.75	2.66	1191	388	0.28	60	4	13	152	1.3	104.8	42	474	6.6	1.3	<0.5	0.4
S-16	17.1	6.76	4.61	828	308	0.38	30	3.5	16.6	113	0	42.5	41.9	376	8.9	1.1	<0.5	0.3
S-21	15.4	7.45	1.72	1372	275	1.70	65.6	3.5	16.5	128	1	150.9	93.1	335	5.5	<0.1	<0.5	0.4
S-22	15.2	7.23	3.08	1164	323	0.17	33	2.5	11.1	139	0.1	105.1	72.5	394	24.6	<0.1	<0.5	0.3
S-23	15.1	6.98	1.96	1129	300	0.12	30.1	2.3	11	181	0.1	122.4	47.4	367	21.1	<0.1	<0.5	0.3
S-24	15.4	6.76	2.21	1115	300	0.13	28.8	2.3	8.95	173	0	124	41.5	367	20.7	<0.1	<0.5	0.3
S-33	14.5	6.82	4.5	776	330	0.18	5.99	1.2	5.44	143	0	39.6	14.5	404	15.6	<0.1	<0.5	0.3
S-36	15.2	6.69	1.67	1300	433	0.16	72.5	4.2	13.1	168	0.8	122.1	42.7	528	19.1	<0.1	<0.5	0.3
S-37	15.8	6.78	4.12	1018	330	1.69	14.3	1.8	6.17	152	0.1	48.6	86.8	401	54.3	<0.1	<0.5	0.3
S-38	18.8	7.39	3.04	578	228	0.19	18.2	2.4	17.6	83.6	0	32.1	26.4	277	3.3	<0.1	<0.5	0.3
S-39	19.7	6.88	4.57	764	328	0.39	21.9	1.4	24.8	102	0	28.4	21.7	400	8.3	<0.1	<0.5	0.3
S-40	18.8	6.85	1.7	1220	220	0.19	57.5	1.6	29.2	78.8	0	130.6	124.5	267	8.7	<0.1	<0.5	0.4
S-41	20.4	6.83	2.16	862	348	0.15	17.3	1.1	29.5	72	0	41.2	33.5	418	14.4	<0.1	<0.5	0.3
TSE 266 (2005)	–	6.5–9.5	–	2500	–	1	200	–	–	–	0.5	250	250	–	50	0.5	–	1.5
EPA (2009)	–	6.5–8.5	–	–														

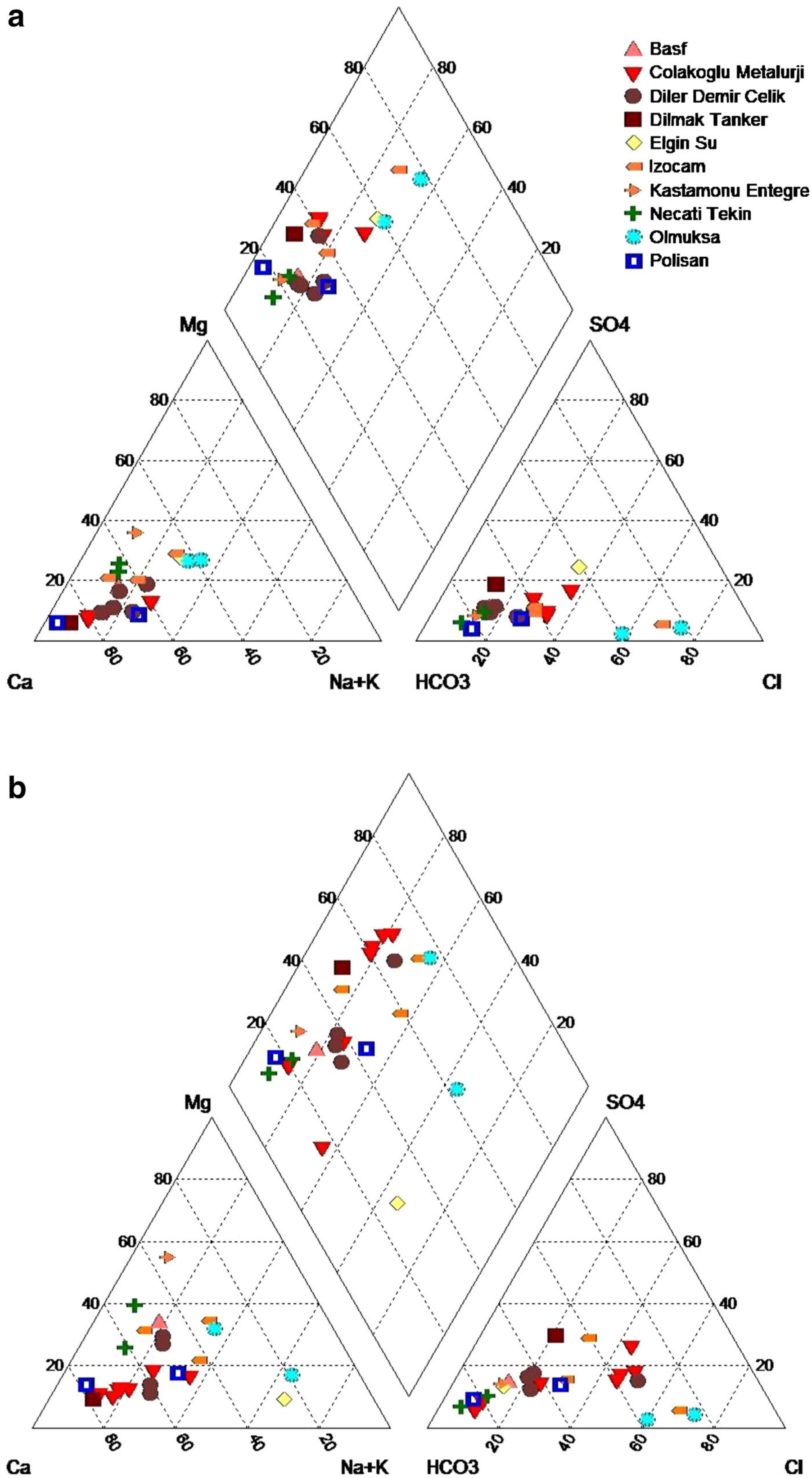

Fig. 6 Piper diagrams of well samples at **a** dry (September 2011) and **b** wet (May 2011) periods

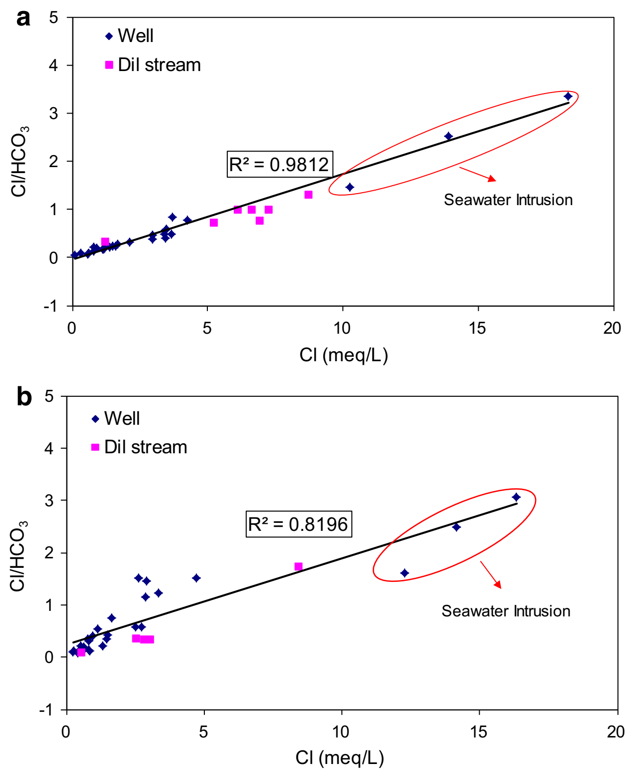

Fig. 7 Variation in Cl vs. Cl/HCO_3 ratios of well and Dil stream water samples at **a** dry (September 2011) and **b** wet (May 2011) periods

To assess the impact of surface water on groundwater quality, the quality of water samples was evaluated according to regulation concerning water intended for human consumption (TSE 266 2005) with regard to the inorganic and microbial parameters measured.

For microbial water quality assessment, total coliform bacteria, *E. coli* and *Enterococci* counts and maximum colony number at 37 °C were used. Total coliform bacteria count is an indicator parameter showing the presence or absence of human pathogens and viruses in water. The existence of *E. coli* and *Enterococci* also indicates fecal contamination from sewage or animal wastes. Due to its high resistance compared to other indicator microorganisms, *Enterococci* is the favored indicator organism for water quality assessment. According to regulation concerning water intended for human consumption (TSE 266 2005), the maximum allowable count for indicator organisms is 0 in 100 mL of water as it is 20 for maximum colony number at 37 °C.

The results of microbiological parameters in groundwater are presented in Table 5 and Figs. 8 and 9. As seen in Table 5, seasonal variation was observed in the microbiological parameter values of the wells. For both sampling periods, S-4, S-6, S-11, S-12, S-14, S-15, S-33, S-36, S-39 and S-41 wells showed microbial contamination for all the indicator parameters examined. Highest values among indicator parameters were seen in *Enterococci*. Depending on sampling period, 40–48 % of the wells showed contamination for *Enterococci*. Only in four wells (S-11, S-14, S-40, S-41) *E. coli* was detected in single sampling period (Table 5). Microbial contamination was observed in dug and deep wells at both upstream and downstream of Dil stream (Figs. 8, 9). These results indicate that the impact of fecal contamination in Dil stream influences deep wells as well. In 20–30 % of wells investigated, turbidity values exceeded also allowable limit of 1 NTU (Table 5).

The groundwater quality in Dilovası alluvial aquifer was also evaluated with regard to metal and nutrient contents according to regulation concerning water intended for human consumption (TSE 266 2005). In the most wells, inorganic parameter values were found below maximum allowable contaminant levels (MCLs). Parameters exceeding MCLs in some wells were NO_3, NO_2, NH_4, Na, Cl and Mn. Dot distribution maps of nutrients and Mn are presented in Figs. 10 and 11.

Nitrate concentrations of groundwater in Dilovası present a wide range of values (Tables 3, 4). Average nitrate concentrations in May and September sampling periods were 24 ± 21 and 17 ± 16 mg/L, respectively. Wells exceeding MCL value (50 mg/L) of nitrate seasonally were S-6 (64.7 mg/L), S-12 (77.6 mg/L) and S-37 (74.7 mg/L) (Tables 3, 4).

NH_4 concentrations in well samples were below MCL (0.5 mg/L) in the 70–84 % of the wells. Seasonally high NH_4 concentrations were detected in S-4 (15.2 mg/L), S-5 (0.5 mg/L), S-11(0.6 mg/L), S-14 (0.8 mg/L), S-15 (1.3 mg/L), S-21 (1 mg/L), S-36 (0.8 mg/L) and S-40 (0.7 mg/L), wells (Tables 3, 4). Similarly, in 80–82 % of the wells investigated, nitrite concentration levels were below MCL (0.5 mg/L). Seasonally, well samples having high nitrite concentrations above MCL were S-5 (1.1 mg/L), S-14 (1.1 mg/L), S-15 (1.3 mg/L) and S-16 (1.1 mg/L) in September; S-7 (1.3 mg/L), S-22 (1.1 mg/L), S-36 (3.4 mg/L), S-37 (1.1 mg/L) and S-40 (2.1 mg/L) in May (Tables 3, 4).

As seen in Fig. 10, recharge from Dil stream, which is highly polluted with wastewater discharges and sewages from residential area, and leachates from old wild landfill at upstream is considered as a source for high nitrate, nitrite and ammonium concentrations in well samples. Relatively high ammonium and nitrite concentrations detected in

Table 5 Results of microbiological parameters in well samples

Well no	Turbidity (NTU) May 2011	Turbidity (NTU) September 2011	Total coliform May 2011	Total coliform September 2011	*E. coli* May 2011	*E. coli* September 2011	*Enterococci* May 2011	*Enterococci* September 2011	Max. colony (37 °C 48 h) May 2011	Max. colony (37 °C 48 h) September 2011
S-2	0.26	0.7	0	0	0	0	0	0	17	5
S-4	4.35	43.2	0	0	0	0	0	0	16	30
S-5	5.42	0.45	0	0	0	0	0	0	95	0
S-6	0.36	0.4	0	>50	0	0	10	18	22	33
S-7	0.21	0.21	0	0	0	0	0	0	10	9
S-8	0.35	0.3	0	3	0	0	0	0	1	0
S-11	0.38	0.31	0	20	0	4	27	7	37	>100
S-12	0.78	0.23	0	0	0	0	32	10	>100	>100
S-14	0.26	0.2	0	15	0	4	16	19	1	>100
S-15	0.27	0.28	0	34	0	0	1	5	50	>100
S-16	–	0.38	–	8	–	0	–	4	–	58
S-21	1.04	1.7	0	>50	0	0	0	0	0	>100
S-22	0.3	0.17	0	0	0	0	0	0	0	0
S-23	0.27	0.12	0	0	0	0	0	0	0	4
S-24	0.19	0.13	0	0	0	0	0	0	0	0
S-25	0.3	–	0	–	0	–	0	–	0	–
S-26	0.53	–	0	–	0	–	0	–	0	–
S-27	0.3	–	0	–	0	–	5	–	7	–
S-33	0.57	0.18	0	8	0	0	2	4	0	7
S-36	0.46	0.16	0	30	0	0	51	0	13	93
S-37	1.16	1.69	0	0	0	0	0	1	0	0
S-38	0.46	0.19	0	0	0	0	17	0	50	8
S-39	0.18	0.39	0	40	0	0	5	1	16	>100
S-40	7.65	0.19	3	0	3	0	0	0	4	4
S-41	0.96	0.15	30	0	27	0	32	0	11	51

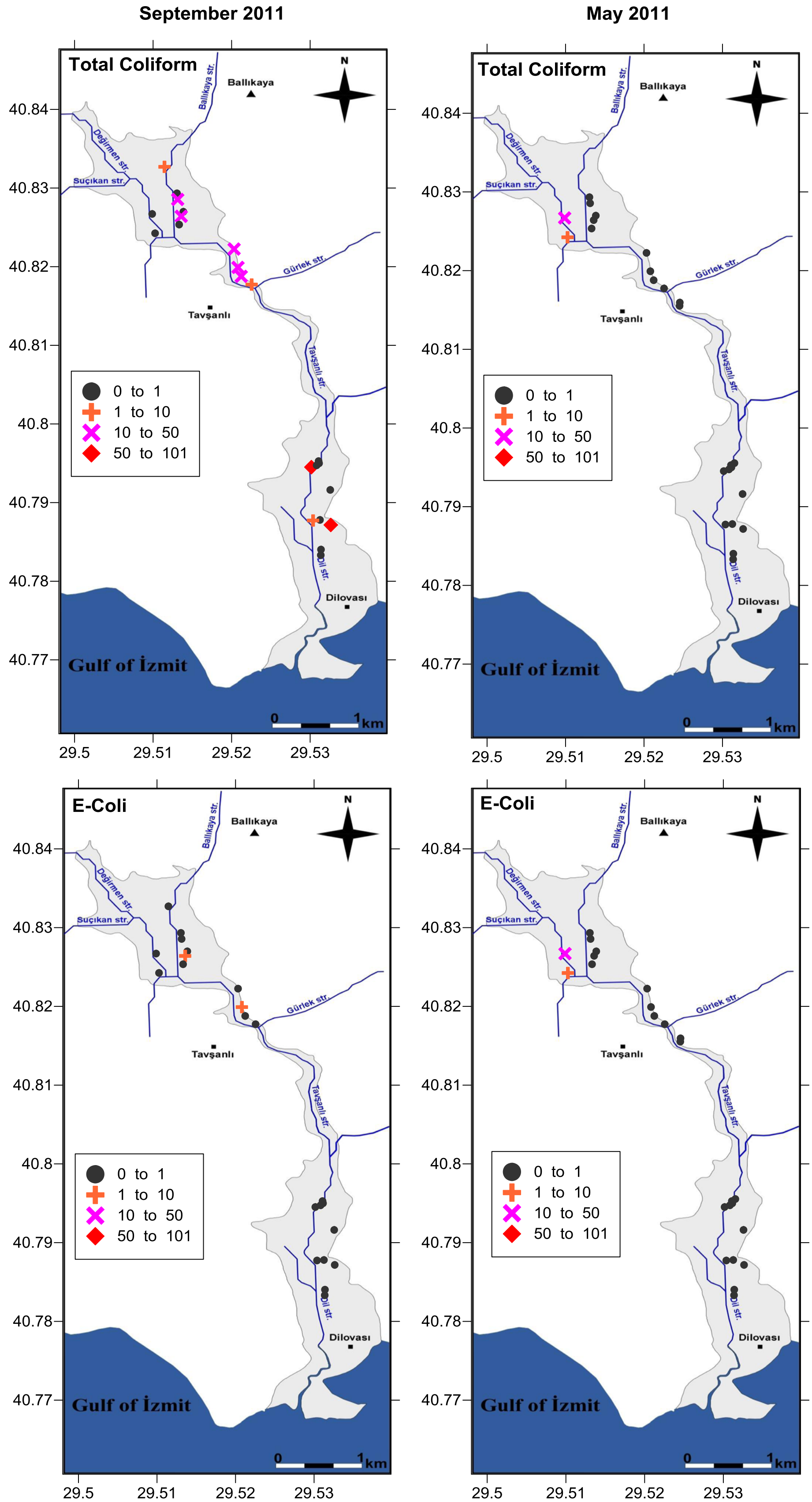

Fig. 8 Dot distribution maps of total coliform and *E. coli* contents of well water samples along Dil stream in dry and wet sampling periods

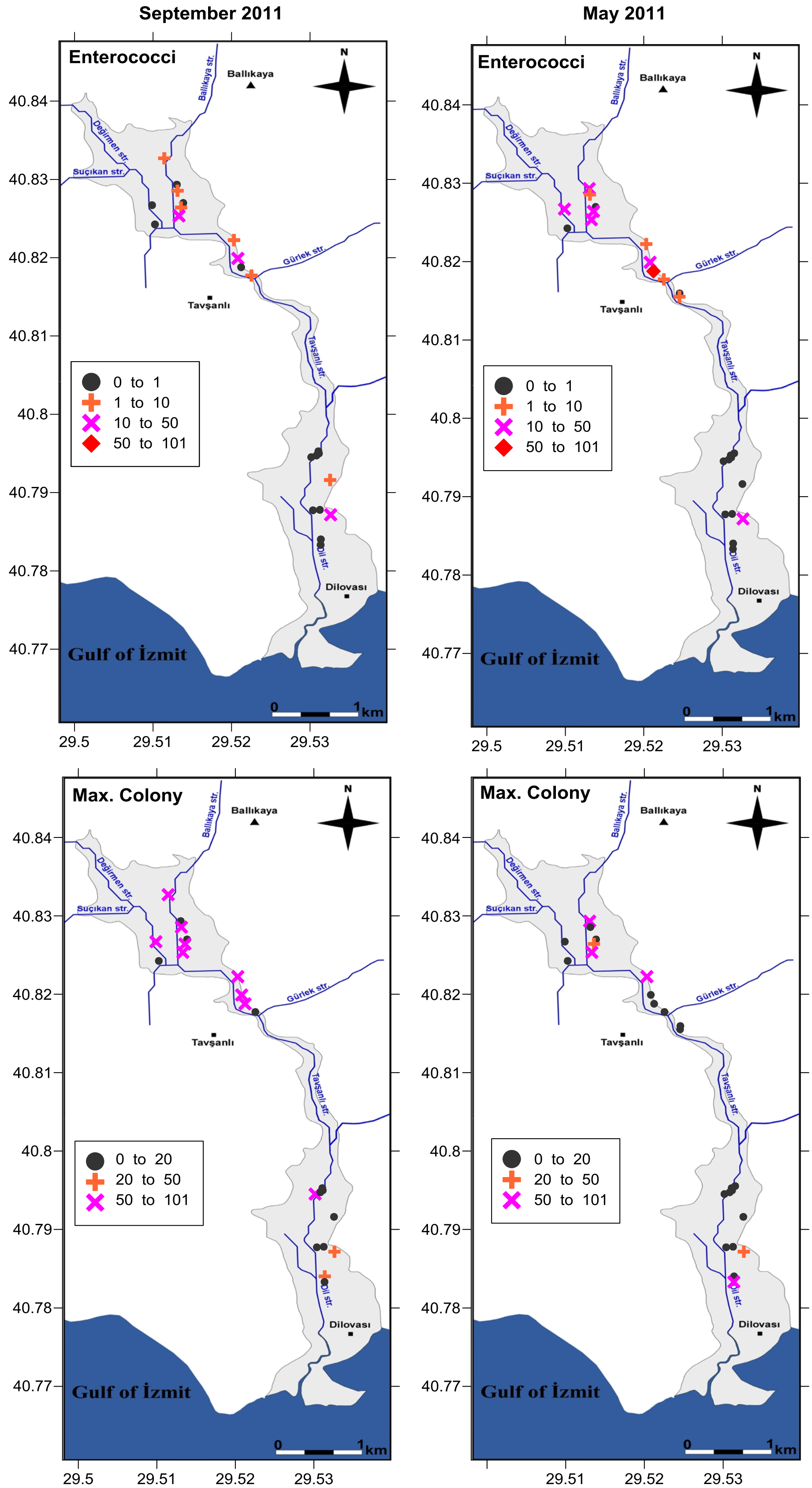

Fig. 9 Dot distribution maps of *Enterococci* and Max. Colony (37 °C) numbers of well water samples along Dil stream in dry and wet sampling periods

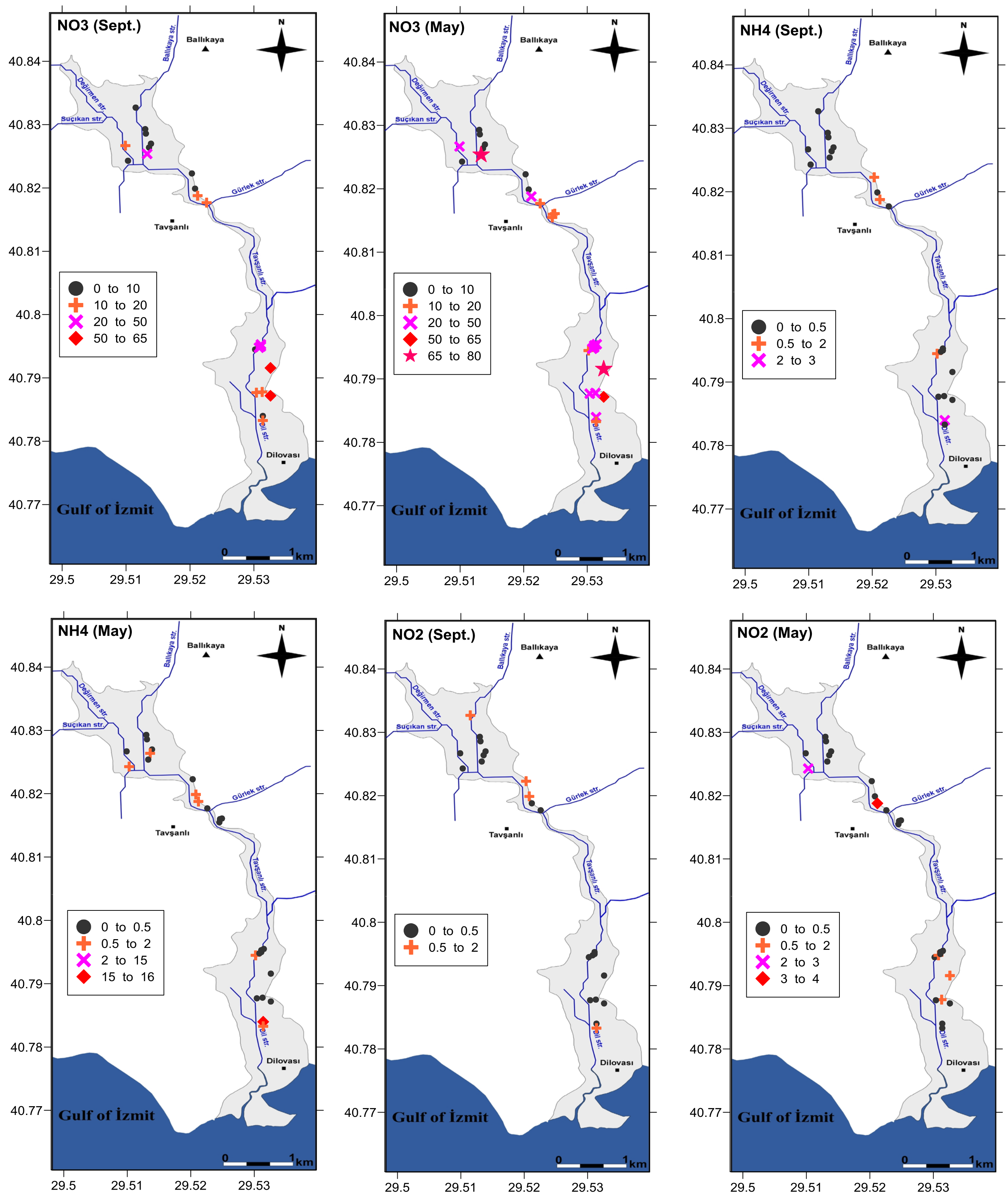

Fig. 10 Dot distribution maps of NO_3, NO_2 and NH_4 contents (mg/L) of well water samples along Dil stream in dry and wet sampling periods

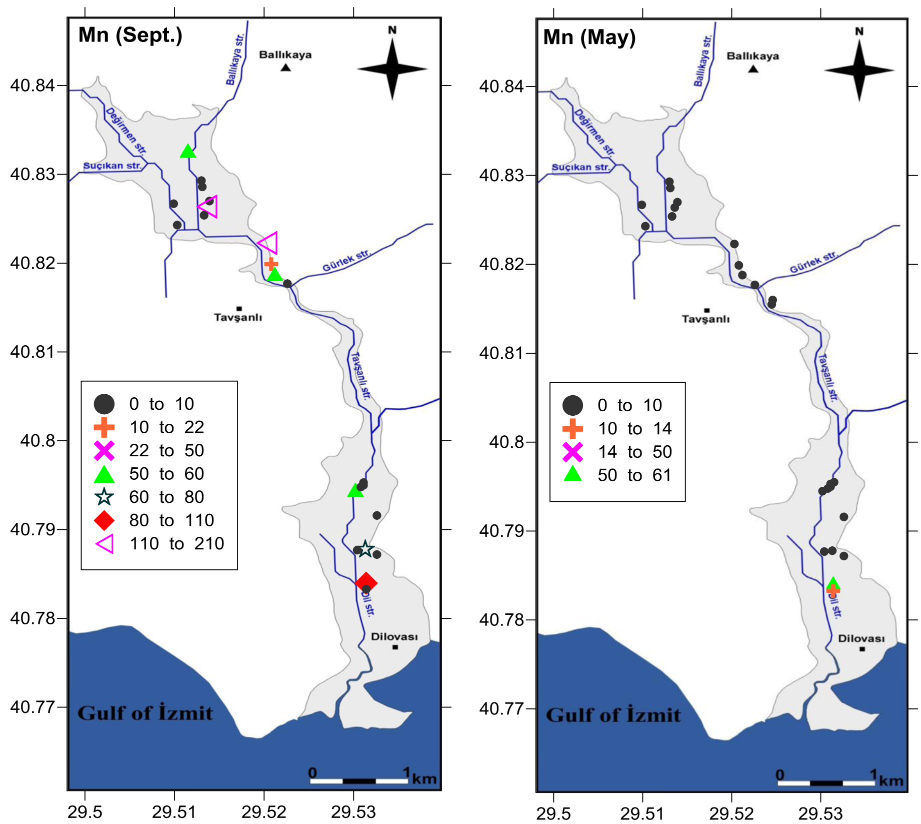

Fig. 11 Dot distribution maps of Mn contents (μg/L) of well water samples along Dil stream in dry and wet sampling periods

stream samples at the upstream and downstream of Dil stream support this argument (Fig. 10; Tables 3, 4).

Metal concentrations of the well samples were also mostly below their MCLs. Only for manganese element, seven well samples [S-4 (105 μg/L), S-7 (79 μg/L), S-11 (124 μg/L), S-15 (208 μg/L), S-16 (55 μg/L), S-21(58 μg/L) and S-36 (55 μg/L)] in dry sampling period showed concentrations above MCL value of 50 μg/L (Fig. 11; Table 6). In May sampling S-4 had a high Mn concentrations (60.7 μg/L) above MCL while in the rest of wells Mn levels were below detection limit (0.01 μg/L) (Fig. 11; Table 7). Although Dil stream is heavily contaminated with respect to Al and Fe, low Al and Fe levels below their MCLs in well samples suggest that these metals were sorbed to the suspended particles of the stream water and not easily bioavailable .

In Dilovası alluvial aquifer, evidences of halo-organic contamination resulting from chemical industries were also investigated by conducting adsorbable organic halogens (AOX) sampling in wells. The presence of AOX in groundwater above background values suggests contamination with halogenated organic compounds such as chlorinated solvents, fenols and pesticides, and PCB (Gron 1993). For this purpose, dug and deep wells selected at the upgradient and downgradient of aquifer along Dil stream were sampled for AOX in only single period (May 2011). Results and dot distribution map of AOX values in groundwater are given in Table 8 and Fig. 12. Most wells located at the upstream of industrial activities exhibited AOX concentration below detection limit (3.5 μg/L). High AOX concentrations were detected in wells at the downstream part of Dil stream where industrial activities were highly populated (Fig. 12). These were S-4 (10.32 μg/L), S-5 (16.7 μg/L), S-7 (11.6 μg/L) and S-37 (8 μg/L) deep wells and S-21 (9.5 μg/L) and S-22 (9.8 μg/L) dug wells (Fig. 12). These results suggest that sign of organic contamination with chlorinated hydrocarbons was present in alluvial aquifer and additional sampling study is needed for determining type of specific organic contaminants.

Conclusions

The impact of uncontrolled industrialization and urbanization on surface and groundwater quality was examined with regard to source, types and levels of contaminants.

Table 6 Metal contents of well samples in dry (September 2011) sampling period

Well no	Al (µg/L)	As (µg/L)	B (mg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (µg/L)	Fe (µg/L)	Mn (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	Sb (µg/L)	Se (µg/L)	Zn (µg/L)	Tl (µg/L)
S-2	1.32	0.35	0.06	<0.01	0.05	0.87	0.011	<0.1	1.05	0.39	2.84	0.59	0.07	0.28	0.65	0.002
S-4	0.15	6.04	0.08	<0.01	0.16	1.76	<0.01	12.4	105	0.53	5.97	<0.01	0.03	5.30	418	0.06
S-5	0.03	6.20	0.07	<0.01	0.15	1.54	0.022	<0.1	4.78	0.65	6.49	<0.01	0.04	5.97	4.61	0.55
S-6	0.94	2.78	0.11	<0.01	0.09	0.49	<0.01	<0.1	0.23	0.38	6.06	<0.01	0.05	1.52	0.92	0.24
S-7	0.11	1.99	0.33	<0.01	0.07	0.85	<0.01	<0.1	79	1.08	9.54	0.08	0.05	1.33	8.53	0.34
S-8	0.01	5.65	0.09	0.024	0.10	1.46	<0.01	<0.1	9.06	2.75	14.60	0.19	0.21	5.17	126	1.98
S-11	0.52	0.77	0.06	0.01	0.06	1.03	<0.01	<0.1	124	0.37	3.50	0.06	0.06	0.33	5.92	0.005
S-12	0.84	1.08	0.03	<0.01	0.04	0.49	<0.01	<0.1	1.01	0.09	4.64	<0.01	0.04	0.44	17.8	<0.001
S-14	1.14	0.84	0.06	<0.01	0.10	0.92	<0.01	<0.1	21.40	0.24	4.41	<0.01	0.05	0.21	1.38	0.015
S-15	0.74	1.21	0.07	<0.01	0.06	1.43	<0.01	<0.1	208	0.43	5.61	<0.01	0.05	0.19	1.55	0.009
S-16	2.10	0.55	0.05	<0.01	0.06	0.69	<0.01	<0.1	55	0.30	2.88	<0.01	0.05	0.17	1.51	0.001
S-21	0.08	1.74	0.11	<0.01	0.04	0.83	0.020	<0.1	58	0.31	4.68	0.01	0.03	1.98	0.55	0.003
S-22	0.06	1.03	0.10	<0.01	0.04	0.30	<0.01	<0.1	4.72	0.13	3.67	<0.01	0.02	2.37	0.41	<0.001
S-23	0.09	1.33	0.07	<0.01	0.04	0.29	<0.01	<0.1	2.70	0.12	3.32	<0.01	0.02	3.22	0.21	<0.001
S-24	0.33	1.39	0.07	<0.01	0.05	0.29	<0.01	<0.1	0.18	0.08	3.35	<0.01	0.02	3.66	0.11	<0.001
S-33	0.45	0.75	0.01	<0.01	0.09	0.23	<0.01	<0.1	0.01	0.03	2.27	<0.01	0.03	0.40	0.02	0.001
S-36	0.17	0.69	0.08	0.01	0.07	1.73	0.089	<0.1	55	0.24	6.37	0.04	0.04	0.16	1.06	0.01
S-37	0.44	0.63	0.07	<0.01	0.02	0.30	<0.01	<0.1	7.74	0.12	2.98	<0.01	0.01	1.84	0.10	0.007
S-38	1.03	0.41	0.02	<0.01	0.05	0.51	<0.01	<0.1	0.32	0.35	1.62	<0.01	0.05	0.10	7.44	0.005
S-39	0.35	0.62	0.07	<0.01	0.14	0.37	<0.01	<0.1	0.99	0.41	1.85	<0.01	0.04	0.18	26.1	0.03
S-40	0.30	0.78	0.09	<0.01	0.03	0.43	<0.01	<0.1	0.16	0.41	6.79	<0.01	0.05	1.05	2.03	0.04
S-41	0.58	0.82	0.03	<0.01	0.13	0.25	<0.01	<0.1	0.20	0.08	2.13	<0.01	0.02	0.43	16.5	0.050
TSE 266 (2005)	200	10	1	5	50	2000	1	200	50	–	20	10	5	10	–	–
EPA (2009)	200	10	–	5	100	1300	2	300	50	–	–	15	6	50	5000	2

Table 7 Metal contents of well samples in wet (May 2011) sampling period

Well no	Al (µg/L)	As (µg/L)	B (mg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (µg/L)	Fe (µg/L)	Mn (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	Sb (µg/L)	Se (µg/L)	Zn (µg/L)	Tl (µg/L)
S-2	0.44	0.23	0.04	<0.01	0.07	0.70	<0.01	<0.1	<0.01	0.28	1.56	<0.01	0.06	0.56	0.38	0.001
S-4	<0.01	2.03	0.36	<0.01	0.20	2.26	<0.01	<0.1	60.7	0.58	2.11	<0.01	<0.01	3.00	3.46	0.022
S-5	<0.01	8.08	0.06	<0.01	0.21	2.81	<0.01	<0.1	13.50	0.64	6.57	<0.01	0.04	6.95	191	0.64
S-6	<0.01	2.30	0.18	<0.01	0.07	0.36	<0.01	<0.1	<0.01	0.43	5.40	<0.01	0.05	1.65	2.51	0.23
S-7	<0.01	1.63	0.48	<0.01	0.05	0.67	<0.01	<0.1	<0.01	1.78	9.91	<0.01	0.07	0.92	0.52	0.44
S-8	<0.01	4.37	0.16	0.01	0.21	1.11	<0.01	<0.1	<0.01	3.67	11.60	<0.01	0.25	7.00	0.36	2.09
S-11	<0.01	0.58	0.06	<0.01	0.05	1.44	<0.01	<0.1	<0.01	0.42	2.07	<0.01	0.09	0.44	2.56	0.007
S-12	<0.01	1.84	0.08	<0.01	0.16	0.56	<0.01	<0.1	<0.01	0.17	3.94	<0.01	0.06	0.86	0.44	0.001
S-14	<0.01	1.13	0.12	<0.01	0.13	0.91	<0.01	<0.1	<0.01	0.29	5.92	<0.01	0.06	0.49	0.22	0.03
S-15	<0.01	0.68	0.06	<0.01	0.09	0.85	<0.01	<0.1	<0.01	0.46	2.98	<0.01	0.07	0.54	0.17	0.006
S-21	<0.01	1.48	0.21	<0.01	0.07	1.03	<0.01	<0.1	<0.01	0.57	6.05	<0.01	0.05	3.32	0.34	0.004
S-22	<0.01	1.10	0.20	<0.01	0.10	0.43	<0.01	<0.1	<0.01	0.22	4.58	<0.01	0.02	4.23	0.22	0.001
S-23	<0.01	1.29	0.16	<0.01	0.10	0.40	<0.01	<0.1	<0.01	0.18	3.56	<0.01	0.03	5.85	0.18	<0.001
S-24	<0.01	1.21	0.14	<0.01	0.11	0.37	<0.01	<0.1	<0.01	0.13	3.77	<0.01	0.03	5.70	0.18	<0.001
S-25	<0.01	1.36	0.15	<0.01	0.12	0.40	<0.01	<0.1	<0.01	0.15	3.49	<0.01	0.03	6.01	0.13	<0.001
S-26	<0.01	0.70	0.06	<0.01	0.10	0.31	<0.01	<0.1	<0.01	0.28	1.99	<0.01	0.06	0.68	<0.01	<0.001
S-27	<0.01	1.01	0.13	<0.01	0.06	0.49	<0.01	<0.1	0.14	0.33	3.21	<0.01	0.07	1.19	0.06	0.006
S-33	<0.01	0.37	0.02	<0.01	0.14	0.12	<0.01	<0.1	<0.01	0.04	1.74	<0.01	0.04	0.63	<0.01	0.002
S-36	<0.01	0.50	0.09	<0.01	0.06	0.87	<0.01	<0.1	<0.01	0.97	4.87	<0.01	0.06	0.54	0.01	0.007
S-37	<0.01	0.74	0.17	<0.01	0.04	0.38	<0.01	<0.1	<0.01	0.19	4.55	<0.01	0.02	4.24	0.16	0.01
S-38	<0.01	1.05	0.06	<0.01	0.12	0.22	<0.01	<0.1	<0.01	0.24	1.88	<0.01	0.04	0.46	<0.01	0.04
S-39	<0.01	0.52	0.04	<0.01	0.13	0.52	<0.01	<0.1	<0.01	0.57	2.62	<0.01	0.10	0.29	0.05	0.001
S-40	<0.01	0.48	0.49	0.01	0.01	1.24	<0.01	<0.1	2.66	2.83	1.70	<0.01	0.03	0.33	410	0.003
S-41	<0.01	0.92	0.02	<0.01	0.17	0.12	<0.01	<0.1	<0.01	0.08	1.51	<0.01	0.02	0.71	7.55	0.05
TSE 266 (2005)	200	10	1	5	50	2000	1	200	50	–	20	10	5	10	–	–
EPA (2009)	200	10	–	5	100	1300	2	300	50	–	–	15	6	50	5000	2

Table 8 AOX concentrations of well samples at wet (May 2011) sampling period

Well no	*X*	*Y*	AOX (μg/L)
S-4	29.5314	40.7840	10.32
S-5	29.5314	40.7833	16.70
S-6	29.5326	40.7872	6.60
S-7	29.5313	40.7878	11.60
S-8	29.5304	40.7877	7.40
S-9[a]	29.5434	40.7789	<3.50
S-10[a]	29.5456	40.7775	<3.50
S-17[a]	29.5440	40.7749	4.10
S-12	29.5133	40.8254	<3.50
S-14	29.5208	40.8199	4.90
S-17	29.5440	40.7749	4.10
S-21	29.5302	40.7945	9.50
S-22	29.5308	40.7948	9.80
S-23	29.5311	40.7950	6.08
S-24	29.5311	40.7953	5.10
S-25	29.5315	40.7955	3.70
S-26	29.5246	40.8160	<3.50
S-27	29.5245	40.8155	<3.50
S-36	29.5212	40.8188	6.58
S-37	29.5326	40.7916	8.00

[a] Represents the wells screened in clayey limestone only in Dilovası and used for baseline value. These wells were not plotted in Fig. 12

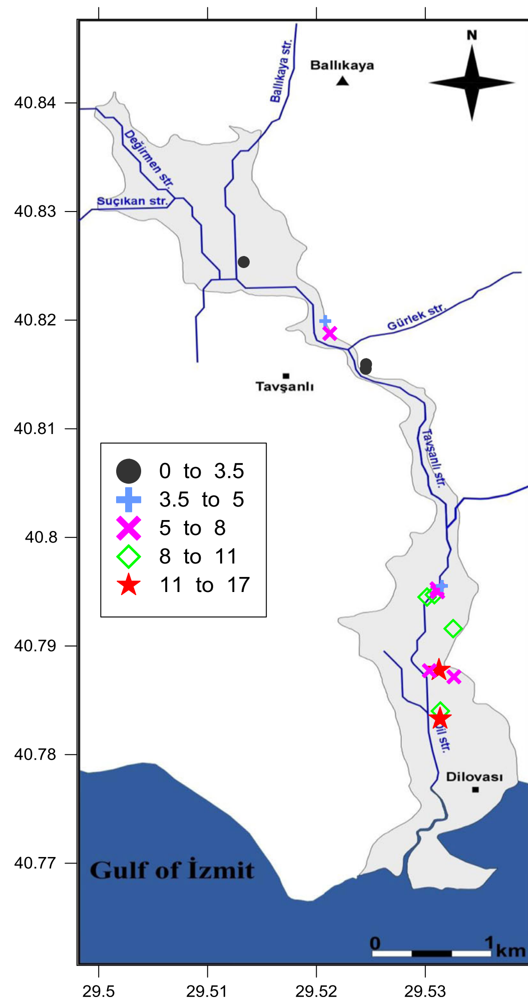

Fig. 12 Dot distribution maps of AOX contents (μg/L) of well water samples along Dil stream in wet sampling period

Results showed that deep wells located near the Gulf of İzmit were affected by seawater intrusion. Microbial pollution indicating fecal contamination was present in alluvial aquifer. In addition, contamination with regard to nutrients exists in groundwater. Contribution of highly polluted Dil stream to the groundwater contamination is significant. Evidences of groundwater contamination were evident in dug and deep wells. The presence of AOXs above baseline levels suggests the industrial activities in Dilovası (especially at the downstream part of Dil stream) for the potential source. Dil stream contaminated by industrial discharges and sewages and leachates from an old wild landfill negatively influences the groundwater quality in the alluvial aquifer. To prevent groundwater contamination in Dilovası, illegal discharges to Dil stream must be taken under control. The effect of high levels of Al, Fe, Mn and Pb contamination detected in Dil stream was not noticed in groundwater quality yet. There is a need for regular monitoring of both surface and groundwater quality in Dilovası. Highly polluted Dil stream was one of the main pollutant sources for the Gulf of İzmit. In Dilovası, streambed rehabilitation of Dil stream and construction of advanced domestic wastewater treatment plant were recently started, and are planned to be completed by 2016.

The data obtained from this study will also establish baseline conditions in the region for future monitoring studies.

Acknowledgments This study was funded by Kocaeli Water and Sewerage Department. We thank anonymous reviewers for their constructive comments.

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