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Full Length Research Paper

Detergent and phosphate pollution ın Gediz River, Turkey

Orkide Minareci[1], Meral Öztürk[2], Özdemir Egemen[3] and Ersin Minareci[1*]

[1]Celal Bayar University, Faculty of Sciences and Arts, Department of Biology, 45140, Manisa, Turkey.
[2]Celal Bayar University, Faculty of Education, Department of Science Education, Manisa, Turkey.
[3]Ege University, Faculty of Fisheries, Department of Marine-Inland Water Sciences and Technology, 35100, İzmir, Turkey.

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The Gediz River, located in western Turkey, drains a region with a high population density and a strong economic activity. These factors, together with a lack of facilities for appropriate treatment of domestic and industrial sewage, are putting increasing pressure on water resources. The aim of the present study was to identify point sources of detergent pollution and to assess the surface water quality in the Gediz River by monitoring physicochemical variables. Point sources of wastewater, including some with a high pollution load, were detected in the most populated and industrialized areas of Manisa and Muradiye municipalities. These sources contribute to increasing degradation of water quality observed in the river. Concentrations of anionic detergents and phosphate were 0.084 - 5.592 g m^{-3} and 0.0044 - 0.248 g m^{-3}, respectively. Gediz River is a significant contributor of nutrients to the Aegean Sea.

Key words: Gediz River, pollution, anionic detergent, phosphate, water quality.

INTRODUCTION

In most developing countries, discharges from point sources have increased significantly as a result of industrialization and high living standards. Additionally, excessive nutrient loads to rivers in these countries has been accompanied by untreated wastewater discharges (Smith et al., 1999). The Global Environmental Monitoring System (GEMS) of the United Nations Environmental Program (UNEP) reported heavy pollution in several rivers around the World (Bichi and Anyata, 1999).

Synthetic surface active agents (synthetic surfactants) or detergents, are used in many industries and in everyday life. The main hazard of detergent pollution lays in their effect on water ecosystems as a whole. In the first instance, surfactants may adversely affect microalgae at the lowest trophic level and impact on their function as major suppliers of oxygen to water bodies (Patin, 1985). The given pollutants favor reduction / increase in primary production and result in community structure infringement (Patin, 1985).

Detergents affect receiving aquatic environments by causing foaming, limiting oxygen production, causing eutrophication and presenting a hazard to waters used for potable supply (Vural and Kumbur, 1982). Surface foams may block aeration of water bodies and their decomposition may increase biochemical oxygen demand and thereby deplete dissolved oxygen levels. Moreover, detergent concentrations greater than 0.1 g m^{-3} are toxic to some marine organisms (Gerlach, 1981). Sub-lethal concentrations may affect other life stages of marine organisms, notably ovum and larval stages (Johnston, 1976). Accelerated eutrophication may occur as a result of the phosphorus (P) content of detergents in natural waters. Thus, the combined effects of excessive concentrations of detergents in natural waters may be reduced oxygen concentrations, a change in water colour, increased turbidity and sedimentation, and a decrease in biological activity (Egemen, 2000).

In recent years, streams and lakes of the region have been threatened by increasing population, industrial and

*Corresponding author. E-mail: ersinminareci@gmail.com. Tel. : +90 236 2412151-152. Fax: +90 236 2412158.

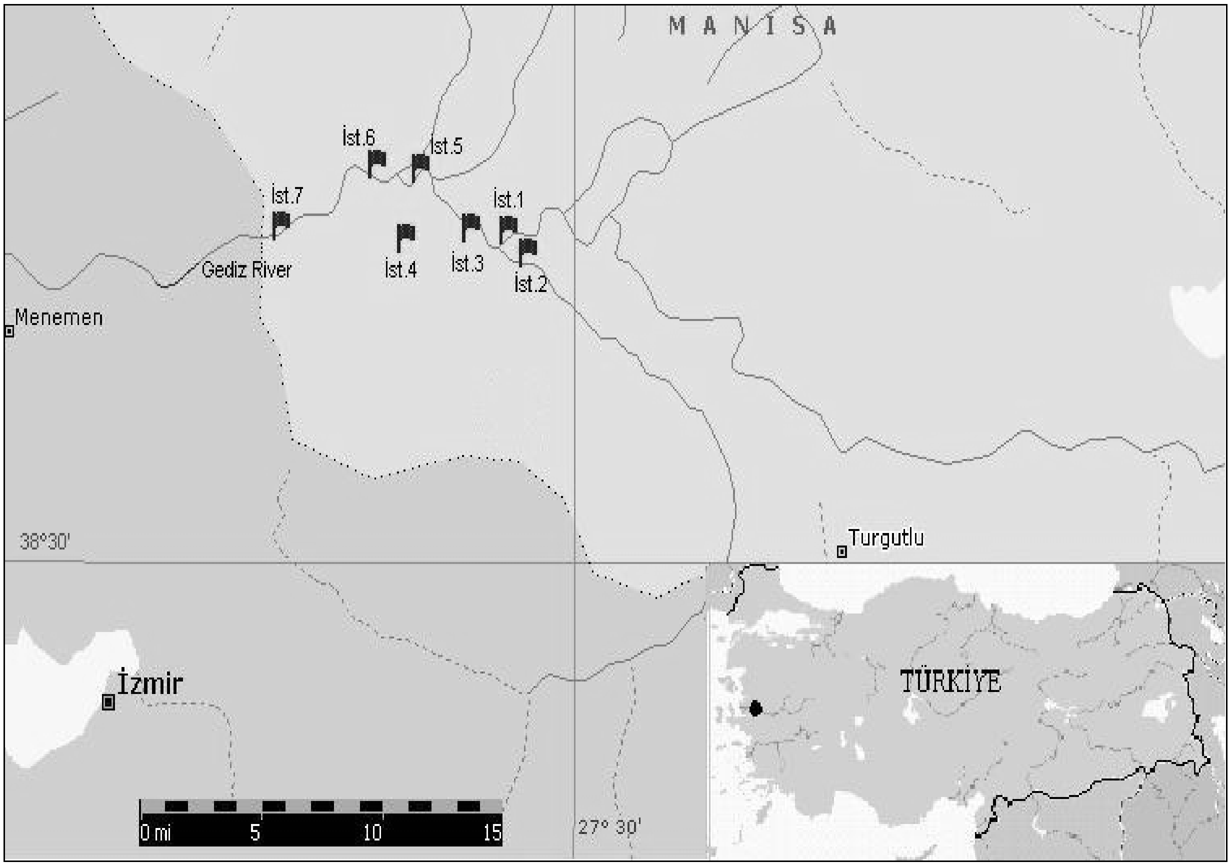

Figure 1. Sampling points.

agricultural activities and non-planned urbanization. Increasing nutrient loading, heavy metal concentrations and feacal bacteria have had a negative impact on the water quality. The most polluted surface water in the region is the Gediz River which rises from the border of Manisa city. The river is an important source of water supply for the city. The Gediz River has been exploited to support agriculture and the public water supply. The major sources of pollutants of Gediz River come from point sources which are point sources that mainly comprise untreated wastewater discharges from organized industrial districts and municipal sewage treatment plants. Diffuse sources mainly comprise runoff from agricultural and forest areas, and from domestic and industrial wastewaters not connected to sewers.

The main problems of the water quality in Gediz River are eutrophication and oxygen depletion. The Gediz River has numerous tributaries and is the main waterway of the city of Manisa. The present study was aimed to investigate detergents and posphorous pollution of Gediz river. Furthermore, analysis of wastewater phosphate showed that 50% originated from urban and industrial sources. Consequently, it is important that ways be found to prevent further inputs from these sources.

MATERIALS AND METHODS

The city of Manisa is located in the western Aegean region and an important agricultural and industrial center of Turkey. The total length of the Gediz River is about 401 km and its basin covers 17500 km^2. In the present study, water samples were taken from seven stations (Figure 1) with positions recorded as GPS coordinates (Table 1).

Samples were collected during the period of June 2005-May 2006. Water temperature, pH, conductivity and turbidity (DKK-TOA product WQC 20A model) were measured at each sampling point at collection. Surface water samples were collected from each location for chemical analyses. Decontaminated bottles (rinsed twice with 50-100 mL tetrahydrofuran or ethyl acetate followed by two rinses with 20-30 mL HPLC grade methanol) were submerged directly below the surface of the water until full. A total of 1 L of surface water were collected at each location to be analyzed for spectrophotometric analysis. Samples of water were transported to the laboratory at 4℃ and analyzed within 1-6 h (Sanderson et al., 2005).

Water samples were prevented from algeal and bacterial effects by adding a chemical composition or mixture comprising a concentrated solution of copper sulfate penta-hydrate ($CuSO_4.5H_2O$), disodium ethylene di-amine tetra-acetic acid dihydrate ($Na_2EDTA.2H_2O$), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), potassium monopersulfate and as much as 15 percent of an acid, such as sulfuric acid (H_2SO_4) (Anonymous, 2002). Anionic and phosphate detergent parameters were analyzed according to Standard Methods (Anonymous, 1995; Parsons et al., 1984).

Table 1. Sampling points and coordinates on Gediz River.

S/N	Station	Coordinate
1	Istanbul Road Gediz Bridge	38''38'39.85'' N, 27''26'47.50'' E
2	Nif Stream	38''38'19.22'' N, 27''27'11.03'' E
3	Manisa Municipality Wastewater Treatment Plant	38''38'43.55'' N, 27''25'0.66'' E
4	Manisa Industrial Wastewater Treatment Plant	38''38'6.02'' N, 27''21'55.04'' E
5	Karaçay	38''40'18.16' N, 27''22'9.59'' E
6	Muradiye Gediz Bridge	38''40'58.59'' N, 27''19'49.28'' E
7	Gediz Izmir Frontier	38''38'2.87'' N, 27''12'23.07'' E

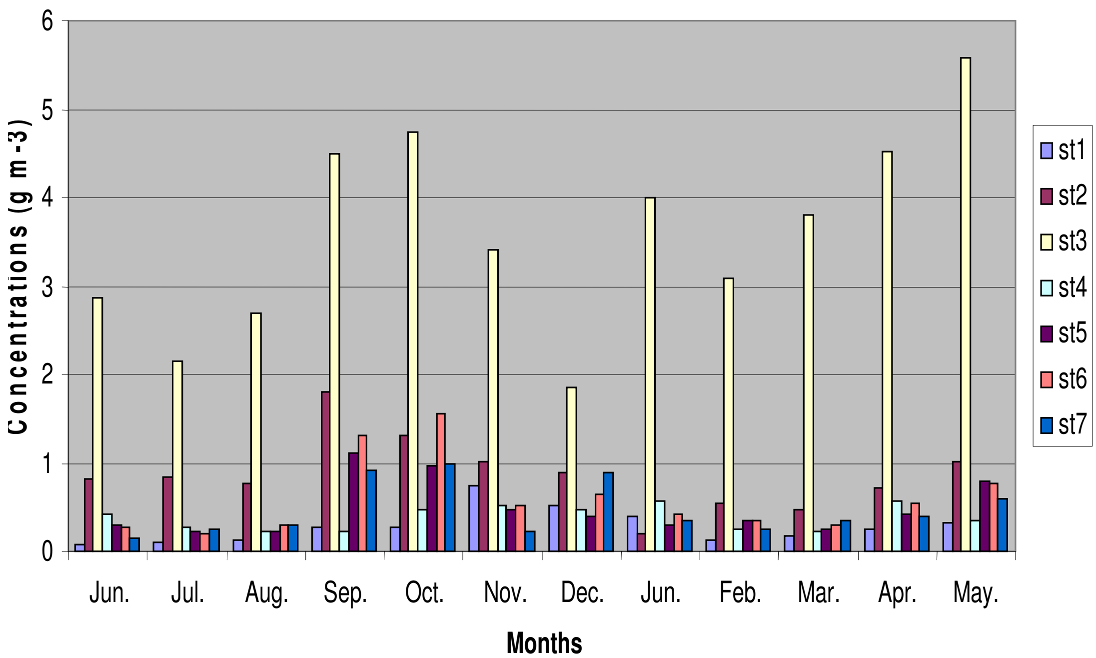

Figure 2. Anionic detergent concentrations of water samples according to sampling date.

Anionic detergent concentration was determined by spectrophotometric analysis of the chloroform soluble phase, resulting from the reaction of methylene blue with surface-active agents (Anonymous, 1995). Phosphate concentration was determined by molybdenum blue colorimetry following ascorbic acid reduction (Parsons et al., 1984). The concentration of anionic detergent and phosphate were determined by spectrophotometric methods at 652 nm and 700 nm, respectively, using a JASCO UV–VIS 530 spectrophotometer.

Windows, Graphad Prism software package was used for statistical analyses. Analysis of variance (one-way ANOVA) was used to determine significance differences existed among stations by detergent and phosphate concentrations and the Tukey test was used to determine significant differences among stations. In addition the "Pearson correlation analysis" method was performed to determine the relationship between anionic detergent and phosphate concentration.

RESULTS

In the present study, anionic detergent and phosphate concentrations were determined monthly at each station over 12 months in 2005-2006. Anionic detergent and phosphate concentration mean values are shown on Figures 2 and 3. In addition pH, temperature, turbidity and conductivity mean values of these samples are presented in Table 2. Relationship between anionic detergent concentrations and physico-chemical parameters was determined by "Linear regression analysis". No linear relation between anionic detergent concentrations and physico-chemical parameters were found ($p > 0.05$).

The one way ANOVA test was used to find if there was a statistically significant difference among the stations. Differences were found for detergent and phosphorus ($p < 0.5$) (Table 3). Applying TUKEY test, Station 3 showed a significant difference compared to all the stations (Table 4). Highest values of detergent and phosphate concentrations were found at Station 3. The one way ANOVA test was used again to find if there was a statis-

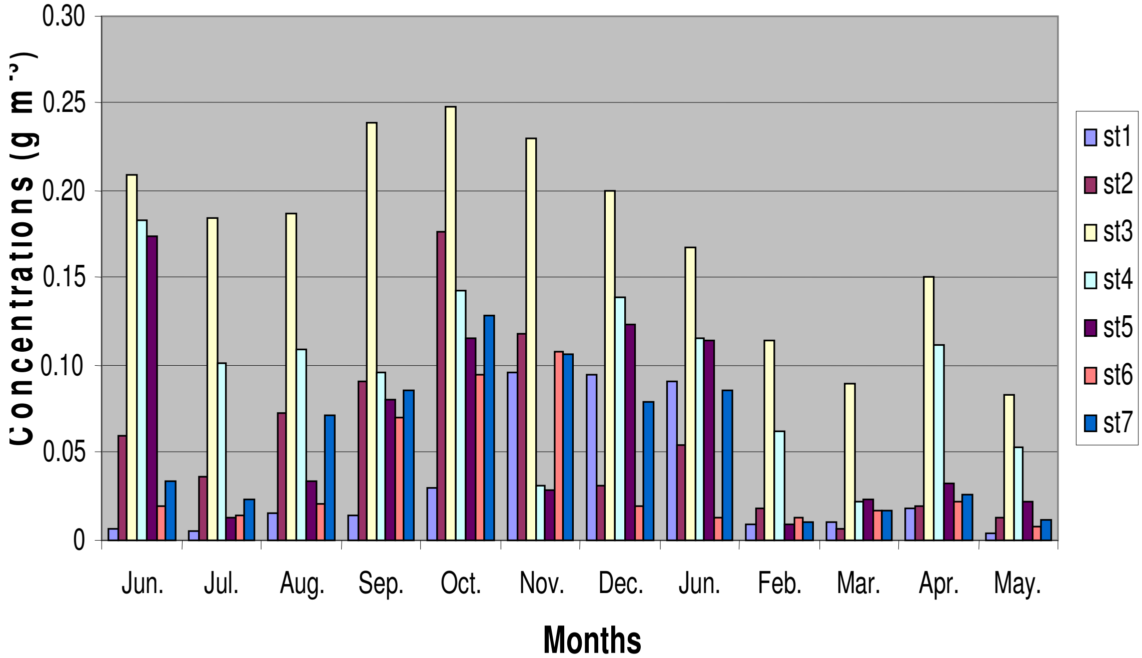

Figure 3. Phosphate concentrations of water samples according to sampling date.

Table 2. Mean values of physico-chemical parameters of sampling stations of Gediz River.

Station		pH	Temperature (ºC)	Turbidity (g m^{-3})	Conductivity (µS)
St.1	Mean ± SD	7.68 ± 0.2	15.95 ± 6.11	462.58 ± 31.06	300 ± 100
	min - max	7.45 – 8.13	4.2 – 23.4	412 – 523	200 – 600
St.2	Mean ± SD	7.6 ± 0.25	16.5 ± 6.62	473.67 ± 119.21	500 ± 300
	min - max	7.17 – 8.05	4 – 25.4	172 – 575	200 – 1000
St.3	Mean ± SD	7.67 ± 0.14	19.46 ± 4.59	448.75 ± 22.7	500 ± 100
	min - max	7.33 – 7.82	12.3 – 25.4	415 – 483	400 – 600
St.4	Mean ± SD	7.61 ± 0.18	26.26 ± 4.1	431.42 ± 20	1700 ± 200
	min - max	7.23 – 7.86	19.3 – 31.6	403 – 464	1400 – 1900
St.5	Mean ± SD	7.8 ± 0.18	18.54 ± 5.71	470.08 ± 19.72	800 ± 300
	min - max	7.54 – 8.14	8 – 26.5	443 – 512	400 – 1200
St.6	Mean ± SD	7.64 ± 0.14	16.89 ± 6.47	492.75 ± 35.88	400 ± 100
	min - max	7.22 – 7.77	4.1 – 25	444 – 571	300 – 700
St.7	Mean ± SD	7.56 ± 0.09	17.23 ± 6.63	465.58 ± 32.36	400 ± 200
	min - max	7.38 – 7.7	4.3 – 25.5	411 – 518	200 – 700

tically significant difference among the months. Differences were not found for detergent and phosphorus ($p > 0.05$).

Dissolved phosphate was significantly correlated to anionic detergent along Gediz River at a 5% significance level as shown in Figure 4 (Anionic detergent and phosphate, $r^2 = 0.79$; $p = 0.007$; $n = 7$).

DISCUSSION

Anionic surfactant and total phosphate concentration guideline limits for surface water (Official Gazete, 2004) were compared with mean concentrations of anionic detergent and phosphate in water samples. From this analysis, waters from the second and sixth stations were class-

Table 3. Results of one-way ANOVA test.

One-way analysis of variance (95% level)	Detergent	Phosphate
P value	P < 0.0001	P < 0.0001
P value summary	***	***
Are means signif. Different? (P < 0.05)	Yes	Yes
Number of groups	7	7
F	63.15	13.46
R squared	0.8311	0.5119

Table 4. Results of Tukey test of detergent and phosphate.

	Parameter	St.1	St.2	St.4	St.5	St.6	St.7
St.3	Detergent	22.34	18.41	21.65	20.97	20.19	21.05
	Phosphate	10.57	8.696	5.785	8.233	10.42	8.791

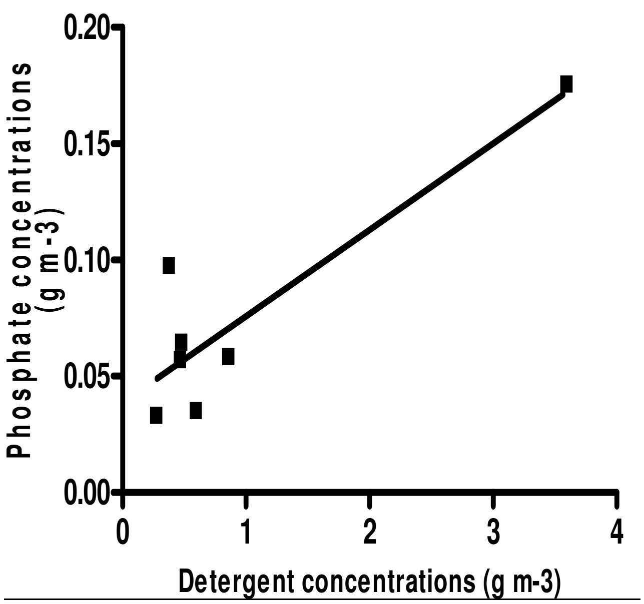

Figure 4. Correlation of dissolved phosphate versus detergent along Gediz River [Det] = 0.015 [Phos] + 0.007.

ified as second class (less polluted water), while waters from the third and fourth stations were classified as 'highly polluted water'. Regarding phosphate concentrations, the third station has the highest phosphate levels and waters were deemed to be 'third class (polluted water)', all others being second class. This is because all of the Manisa Municipality wastewater treatment plant at third station and also detergent contains too much phosphate. In this case, the plant capacity must be developed and wastewater must be discharge after proper purification.

The regulations for wastewater detergent discharge permit a maximum concentration of 0.02 g m^{-3} and samples from the third and fourth stations exceeded this.

Therefore discharge level of detergent of domestic waste-water and industrial wastewater must be decreased. And also possible detergents with low phosphate contents may be used. Furthermore, discharge wastewaters must be discharge into Gediz after proper detergent purifica-tion.

Moreover, according to European Union wastewater quality criteria, reference level of metilen blue active agents is ≤0.3 g m^{-3} and according to the World Health Organization, anionic detergent limit of drinking water is under 0.2 g m^{-3}. As a result of our study we found a high level (average 0.951 g m^{-3}) for Gediz.

The detergent concentrations reported by other researchers on some of the rivers of Turkey and some of the major rivers of the world are summarized in Table 5. The average detergent concentration determined in Gediz River was found to be lower than the rivers of Turkey and but found to be higher than the rivers of the world.

Phosphate concentration sagnificant parameter is in mostly water quality researches. The obtained phosphate values in rivers are shown Table 6. The average phosphate concentration as regards Gediz River was found to be lower than the other studies.

More biodegredable surface active agents must be used for prevention of high detergent and phosphate pollution level of rivers. Detergent contents of sodium tripoli phosphate (STP), used for decreasing water hardness, can be changed with harmless alternatives. Besides wastewater phosphate content can be decreased or phosphate can be removed by chemical or biological ways. Lime, aluminium and ferric salts can be used for purification of phosphorus compounds chemicaly. Phos-

Table 5. Comparison of detergent concentrations in water of different rivers.

River name	Detergent concentration (g m^{-3})	Reference
Ankara Stream (Turkey)	10.24	(Karapars 1976)
Çubuk Stream (Turkey)	11.03	(Karapars 1976)
Ankara Stream (Turkey)	3.37	(Vural and Kumbur 1982)
Melez Stream (Turkey)	5	(Şengül et al. 1986)
Arap Stream (Turkey)	4.8	(Şengül et al. 1986)
Nif Stream (Turkey)	2.155	(Balık and Ustaoğlu 1991)
Melez Stream (Turkey)	0 – 6.93	(İzgören 1992)
Gediz River (Turkey)	0.023 – 4.48	(Tuğrul 1992)
Yuvarlak Stream (Turkey)	0.12	(Balık et al. 2002)
Bakırçay River (Turkey)	0.01 – 0.29	(Başaran 2004)
Küçük Menderes River (Turkey)	0 – 0.93	(Egemen et al. 2005)
Halifax Harbour River (Canada)	0.001 – 0.2	(Gagnon 1983)
England Rivers	0.007 – 0.173	(Waters and Garrigan 1983)
England Rivers	0.012 – 0.08	(Gilbert and Pettigrew 1984)
Tama River (Japan)	0.035 – 0.219	(Yoshikawa et al. 1984)
Hyogo River (Japan)	0.004 – 2.5	(Kobuke 1985)
Tsurumi River (Japan)	0.01 – 0.29	(Yoshikawa et al. 1985)
Sumida River (Japan)	0.005 – 0.01	(Kikuchi et al. 1986)
Saar River (Europa)	0.01 – 0.09	(Matthijs and De Henau 1987)
Teshiro River (Japan)	0.01 – 0.27	(Kojima 1989)
Teganuma River (Japan)	0.019 – 1.4	(Nonaka et al. 1989)
Yodo River (Japan)	0.043 – 0.089	(Nonaka et al. 1990)
Miami River (America)	< 0.05	(Hand et al. 1990)
Oohori River (Japan)	0.5 – 1.6	(Amano et al. 1991)
Mississippi River (America)	0.01 – 0.3	(McAvoy et al. 1993)
Litheos River (Mediterranean)	0.1	(Dassenakis et al. 1998)
Yorkshire River (England)	0.05 – 0.25	(Fox et al. 2000)
Laguna Bay (Filipinler)	0.002 – 0.102	(Eichhorn et al. 2001)
Itter River (Germany)	0.007 – 0.011	(Wind et al. 2004)
Gediz River	0.084 – 5.592	This study

phorus is sedimented as phosphate salts at high pH levels in these processes. Biological purification is made by decomposition of detergents and phosphates by micro-organisms. Because of wastewater plants generally have high organic compound concentrations, micro-organisms increase rapidly. Meanwhile they use nutrients for necessity. Despite most of the microorganisms can adsorbe detergents, level of detergents can be decreased by them. So detergent levels and their toxic effects to the living organisms can be prevent biologicaly at the source of the pollution. Advanced phosphorus clarification can be occured by shallow alg lagoons, algean produce densely and harvest. Harvested algean can be used for biogas production and as a fodder. Phosphorus pollution level of rivers also effected by soil compost. Eutrophication is a danger for Gediz River because of high phosphorus pollution. Therefore, soil charesteristic must be determined. According to these datas, proper sort and amount of compost can be determined.

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Table 6. Comparison of phosphate concentrations in water of different rivers.

River name	Phosphate concentration (g m^{-3})	Reference
Meriç River	0.0001 – 0.02	Kontaş (1990)
Gediz River	0.016 – 4.054	Tuğrul (1992)
Gediz River	0.02 – 7.41	Okur et al. (1997)
Dalaman Stream	0.213	Barlas (1999)
Yuvarlak Stream	0.08	Barlas (1999)
Asi River	0.002 – 2.44	Taşdemir and Göksu (2001)
Yuvarlak Stream	0.02	Balık et al. (2002)
Bakırçay River	0.0018 – 0.0229	Başaran (2004)
Karaçay Stream	0.22– 6.82	Kara and Çömlekçioğlu (2004)
Küçük Menderes River	0 – 1.88	Egemen et al. (2005)
Ankara Stream	3.81	Atıcı and Ahıska (2005)
Cark Stream	0.208	Kurtulmuş (2006)
Rheraya River (Fez)	0.043 – 1.286	Khebiza et al. (2006)
Nhue River (Vietnam)	3.5	Duc et al. (2006)
Dun River (England)	0.086	Neal et al. (2006)
Kenet River (England)	0.083	Neal et al. (2006)
Fuji River (Japan)	0.01 – 0.13	Shrestha and Kazama (2007)
Yangtze River (China)	0.64 – 1.31	Zhang et al. (2007)
Gediz River	0.0044 – 0.248	This study

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