

## Effect of Land Use on Some Physical and Chemical Water Quality Parameters in the Sub-watersheds of Big Melen Stream

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### ABSTRACT

This study was carried out in two watersheds of the Big Melen Stream, which provides water to Istanbul. Forest areas are dominant in the Yukarıkaraköy watershed, whereas agricultural areas (hazelnut plantations) are dominant in the Avlayan watershed. There are settlement areas at the outlet regions of both watersheds. The purpose of the study was to compare the effect on the water quality as a consequence of the forests, settlement areas, and hazelnut plantations. Accordingly, pH, electrical conductivity (EC), dissolved oxygen (DO), total nitrogen (TN), NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, and NH<sub>4</sub><sup>+</sup> concentrations were measured in the stream points representing hazelnut plantations, forests, and settlement areas for 2 years. The water quality classification of the sampling points was determined in accordance with the criteria specified in the Turkish Surface Water Quality Regulations (SWQR). The mean EC, TN, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and DO of the sampling point representing the forest were 264 µS/cm, 1.5 mg/L, 3.1 mg/L, 14.7 mg/L, and 10.3 mg/L, respectively. The mean EC, TN, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> values of the point representing the hazelnut plantation were higher than those of the point representing the forest. In the sampling points representing the settlement areas of both watersheds, the EC and PO<sub>4</sub><sup>3-</sup> increased, while the DO decreased. As a result, it was determined that the stream water of the point representing the forest was of higher quality than that of the point representing the hazelnut plantation and that the settlement areas significantly reduced the water quality by increasing the concentrations of pollutants.

**Keywords:** Big Melen Stream, land use type, nonpoint-source pollution, water quality parameters

### Introduction

Population growth, climate change, urbanization, land-use change, and pesticide and fertilizer usage cause degradation of water quality through point-source and nonpoint-source pollution. In addition to water pollution, human activities and conversion of natural lands for other uses are especially important factors that increase the surface flow and sediment efficiency by changing the soil-vegetation water balance (Elçi & Selçuk, 2013; Florsheim et al., 2011; Keshtkar et al., 2011; Tang et al., 2005). Gathering data to explain the effects of these factors are of great importance for the creation of integrated watershed management plans and sustainable water resource management. The principles necessary to achieve good water status and matters relating to the quality and classification of surface waters in Turkey are included in the Surface Water Quality Regulations (SWQR, 2016).

The cause of nonpoint-source pollution is difficult to control, as it cannot be linked to a single source. In other words, when more than one source causes deterioration of water quality, it is not easy to distinguish the effects of these mixed sources on pollution from one another (Coulter et al., 2004; Wang et al., 2009).

Many researchers have stated that land use activities in a watershed affect the hydrological processes by changing the type of vegetation cover and the physical and chemical properties of the soil and water in the watershed (Johannsen & Armitage, 2010; Wang et al., 2013; Warburton et al., 2012). The hydrological processes are affected because of changes in evapotranspiration, infiltration, interception, surface flow, and subsurface flow in parallel with land-use change (Cui et al., 2012; Keshtkar et al., 2011).

According to the results of studies carried out in many parts of the world, there is a positive correlation between the concentrations of water pollutants and increases in agriculture, settlements, and industry

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(Ahearn et al., 2005; Coulter et al., 2004; Haidary et al., 2013), whereas a negative correlation has been found with the increase of forest areas (Liu et al., 2009; Kibena 2014; Knee & Encalada, 2014; Tu, 2013). However, the results of studies conducted in different regions on the relationship between land use and water quality are not consistent. Because the characteristics, traditions, physical environment, and pollution sources of watersheds are not the same, water quality and land use indicators may differ in watersheds in different regions or different watersheds in the same region (Tu, 2013). For example, in watersheds with similar rainfall and land use, because of differences in hydrological characteristics and soil textures, forested watersheds may have different effects on water quality. However, even if the water quality changes with the change of land use, it may be difficult to determine a direct relationship between the two (Khare et al., 2012).

More than 50% of the water needs of Istanbul, Turkey's most populous province (15 million), are supplied by the Big Melen Stream (Akiner & Akkoyunlu, 2012). The city of Düzce is the largest urban settlement within the watershed. The livelihood of the people is based on agriculture, animal husbandry, industry, and the service sector. Therefore, the watershed is affected by nonpoint-source pollution such as pesticides, fertilizers, and animal waste and point-source pollution such as industrial wastewater (Dogan et al., 2009; Koklu et al., 2010).

This study was carried out in two adjacent sub-watersheds of Big Melen Stream. Approximately 64% (214 ha) of the Yukarıkaraköy watershed is forest and 36% (120 ha) agricultural land, whereas 27% (194) of the Avlayan watershed is forest, 70% (499 ha) agricultural land, and 3% (21 ha) settlement. Most of the agricultural land in the watersheds is used for hazelnut cultivation, and the usage of fertilizers is common in these areas.

The aim of this study was to investigate the effects of forests, hazelnut cultivation, and settlements on water quality in creek watersheds having similar climatic conditions that supply water to the Big Melen Stream. The results of the study will contribute to the sustainable management of the Big Melen watershed, as a source of Istanbul's water, in terms of nonpoint-source pollution and water quality.

## Methods

### Study Watersheds

The study was carried out in Turkey's Western Black Sea Region in the Avlayan and Yukarıkaraköy Creek watersheds, located within the boundaries of Düzce Province between 40° 51' 58"–40° 55' 09" northern latitudes and 30° 58' 02"–31° 02' 08" eastern longitudes (Figure 1). The average annual precipitation and temperature in Düzce are 822.1 mm and 13.3°C, respectively. The highest precipitation occurs between October and January. According to the Thornthwaite method, water shortage is experienced in Düzce in July, August, and September (Çitgez, 2017). The average annual precipitation in the research area for the years measured was 1127.4 mm, and the seasonal precipitation distribution for winter, spring, summer, and autumn was 292.2 mm, 244.4 mm, 264.8 mm, and 326 mm, respectively.

The soil properties of the watersheds are similar, with both having a heavy clay content. The amount of clay increased as the soil depth increased. The mean soil textures found in the Yukarıkaraköy watershed are 31% sand, 23% silt, and 46% clay and in the Avlayan watershed, 33% sand, 18% silt, and 49% clay (Çitgez, 2017). The geological structure of the watersheds consists of sandstone-mudstone, clayey limestone, and sedimentary rock groups. The dominant land use type

in the Avlayan watershed is agriculture (hazelnut cultivation), while the dominant land use type in the Yukarıkaraköy watershed is forest (Figure 1). In both watersheds, settlement-agricultural areas dominate between the watershed outlet and the section where the water flows into the Big Melen Stream. The vegetation of the forest areas consists of broad-leaved forests dominated by Eastern beech (*Fagus orientalis* Lipsky), oak (*Quercus petraea* (Matt.) Liebl.), and hornbeam (*Carpinus betulus* L.) species. Hazelnuts (*Corylus* sp.) are grown in agricultural areas.

The population of Avlayan village is 626 and that of Yukarıkaraköy is 478 (TUIK, 2017). The inhabitants earn their livelihood from agriculture and cattle breeding. Nitrogen and phosphorus-containing fertilizers are mostly used in agricultural areas. According to the information received from the local people, lime and triple superphosphate (42% P<sub>2</sub>O<sub>5</sub>) fertilizer is applied to the soil of the hazelnut plantations every 2–3 years in the winter, while in the spring, urea (46% N) and ammonium sulfate (21% N) fertilizers are applied.

### Sampling and Analyses

In order to investigate the effect of land use on water quality, water samples were taken at least twice a month between December 2013 and November 2015 from four different points of the streams flowing into the Big Melen Stream before and after the settlement area of each watershed. The sampling point in the outlet of the Avlayan watershed (Av-1) represented the hazelnut plantations, and the outlet of the Yukarıkaraköy watershed (Ykr-1) represented the forest areas. The sections where the streams flowed into the Big Melen Stream (Av-2, Ykr-2) represented settlement-agricultural areas (Figure 1). A total of 212 water samples were taken from these four points over the 2 years. Water samples were taken with 0.5-L polyurethane containers and kept in thermoses with ice until chemical analyses were carried out. Analyses were generally performed on the same day. When the analysis could not be done immediately, the samples were kept in the refrigerator at +2°C.

During sampling, electrical conductivity (EC), pH, and dissolved oxygen (DO) measurements were taken using the Hach–Lange HQ40D dual-channel Digital Multiparameter device (Korkanç et al., 2017). The total nitrogen (TN), anion, and cation analyses were performed in the Düzce University Scientific and Technological Research Application and Research Center (DUBIT). The Hach–Lange DR3900 spectrophotometer was used for TN analysis, and the Thermo Scientific Dionex ICS-5000+ ion chromatography system for anion (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) and cation (NH<sub>4</sub><sup>+</sup>) analysis.

### Statistical Analyses

The data measured to examine the impact of different land use on water quality parameters were evaluated separately based on all measurements and seasons (spring, summer, autumn, winter). Analysis of variance (ANOVA) was used to compare the water quality of the sampling points. Before carrying out the analyses, the data were checked to ascertain whether all variables showed normal distribution and whether the variances were homogeneous. A normality check was performed using the Shapiro–Wilk test, and the Levene's test was used to check the homogeneity of the variances. If the ANOVA results were found to be significant ( $p < .05$ ), the Duncan's test was used to compare the means of the variables. The SPSS Statistics-V21.0 software package was used to evaluate all data. The water quality classes of the sampling points were determined according to the SWQR criteria, taking into account all average measurement values of the parameters (Table 1).

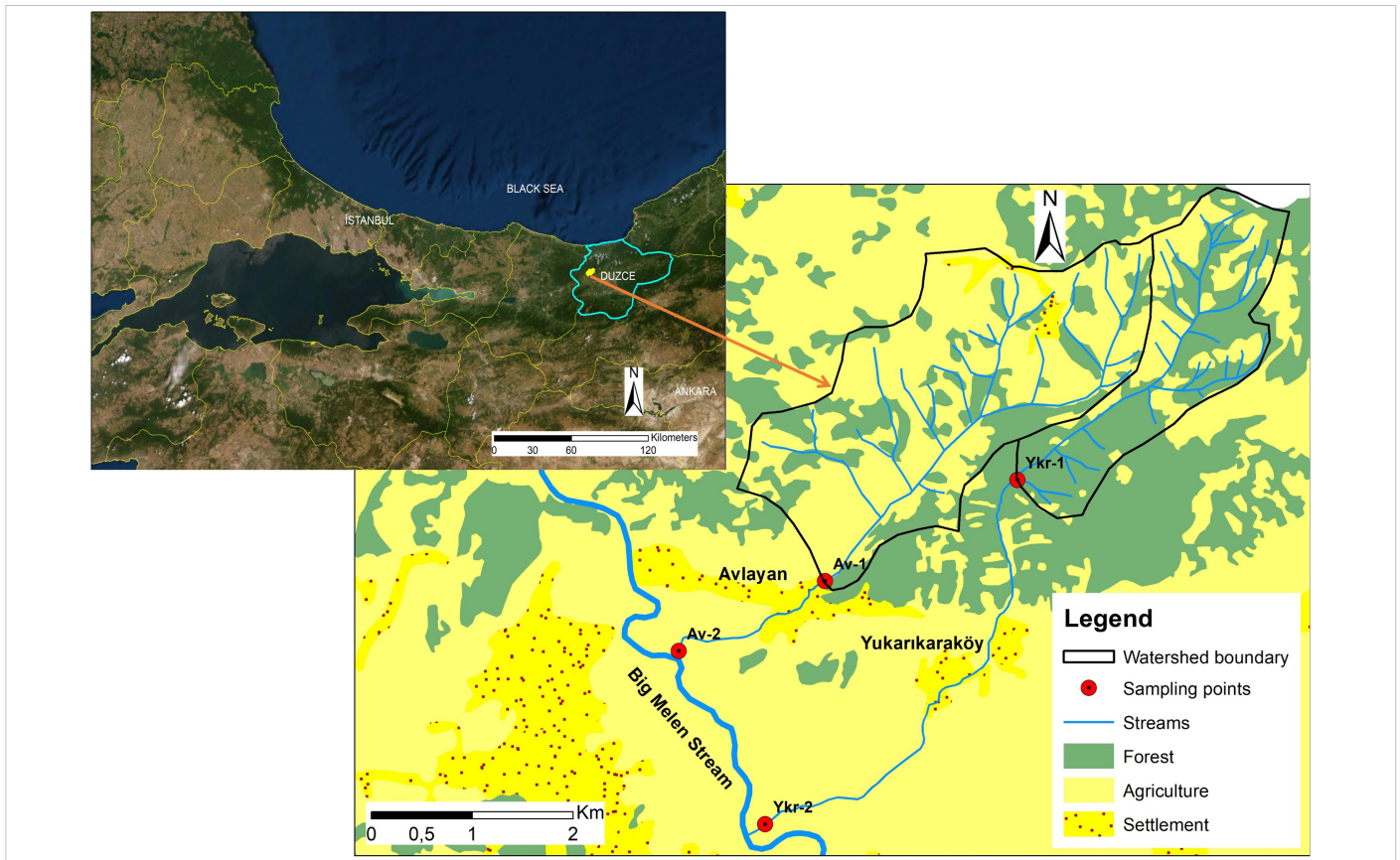


Figure 1. Location of Research Watersheds and Land Use Distribution.

## Results and Discussion

### pH

During the research, the highest monthly average pH (9.2) was measured in Ykr-1 and the lowest (7.9) in Av-2; the water of the watersheds was basic. Calcareous bedrock in the watersheds may have had an effect on the basic nature of the water. According to all measurement averages, no difference was found between Ykr-1 and Av-1 in terms of pH. Although the pH of Ykr-2 was lower than in Ykr-1, the pH of Av-2 was found to be similar to Av-1 (Table 2). The low pH in Ykr-2

was thought to have been caused by animal waste from the adjacent pasture as mentioned in the study of Suratman et al. (2016).

A difference was found between the points only in the winter season, and the pH of the points decreased steadily from winter to spring, summer, and autumn (Table 3). This may have been a result of increased CO<sub>2</sub> production caused by the decomposition process. As mentioned in the study of Suratman et al. (2016), the decrease in DO following the winter season suggests that the decomposition of organic substances

Table 1. Water Quality Classification of Surface Water Quality Regulations (SWQR, 2016)

Parameters	Water Quality Classes			
	1 (High Quality)	2 (Slightly Polluted)	3 (Polluted)	4 (Highly Polluted)
pH	6–9	6–9	6–9	6–9
EC (µS/cm)	<400	1000	3000	>3000
DO (mg/L)	>8	6	3	<3
TN (mg/L)	<3.5	11.5	25	>25
NO <sub>3</sub> -N (mg/L)	<3	10	20	>20
Total Phosphorus (mg/L)	<0.08	0.2	0.8	>0.8
NH <sub>4</sub> -N (mg/L)	<0.2	1	2	>2

Table 2. Overall Mean Values of Water Quality Parameters at Sampling Points

Parameters	Sampling Points			
	Ykr-1 (Forest)	Ykr-2 (Settlement)	Av-1 (Hazelnut Plantation)	Av-2 (Settlement)
pH	8.5 (0.30)b*	8.4 (0.26)a	8.5 (0.25)b	8.5 (0.26)b
EC (µS/cm)	264 (78)a	408 (92)b	437 (78)b	471 (90)c
DO (mg/L)	10.3 (1.1)b	9.6 (1.7)a	9.9 (1.2)a,b	9.3 (1.7)a
TN (mg/L)	1.5 (1.7)a	2.3 (2.3)a	3.3 (2.0)b	4.4 (2.1)c
NO <sub>2</sub> (mg/L)	0.04 (0.08)a	0.12 (0.14)a	0.15 (0.44)a	0.66 (0.77)b
NO <sub>3</sub> (mg/L)	3.1 (2.7)a	4.3 (3.0)a	9.9 (6.3)b	10.5 (6.1)b
SO <sub>4</sub> (mg/L)	14.7 (4.0)a	17.4 (4.7)b	23.0 (6.5)c	22.4 (6.3)c
PO <sub>4</sub> (mg/L)	0.17 (0.15)a	0.3 (0.22)b	0.17 (0.15)a	0.54 (0.25)c
NH <sub>4</sub> (mg/L)	0.08 (0.26)a	0.67 (0.89)a	0.37 (1.50)a	3.16 (3.23)b

Note: Means with the same letter in rows are not significantly different ( $p > .05$ ). The standard deviation is shown in parentheses.

**Table 3.**  
**Seasonal Mean Values of Water Quality Parameters at Sampling Points**

Parameters	Sampling Points	Winter	Spring	Summer	Autumn
pH	Ykr-1	8.64 (0.3)a,b*,B**	8.49 (0.3)a,A,B	8.43 (0.3)a,A,B	8.33 (0.3)a,A
	Ykr-2	8.50 (0.2)a,B	8.42 (0.3)a,A,B	8.30 (0.2)a,A	8.28 (0.2)a,A
	Av-1	8.68 (0.2)b,C	8.56 (0.3)a,B,C	8.40 (0.2)a,A,B	8.37 (0.2)a,A
	Av-2	8.71 (0.2)b,B	8.57 (0.3)a,B	8.32 (0.2)a,A	8.36 (0.1)a,A
EC (µS/cm)	Ykr-1	230 (74)a,A	238 (70)a,A	296 (80)a,B	307 (66)a,B
	Ykr-2	392 (100)b,A	424 (102)b,A	384 (79)b,A	430 (85)b,A
	Av-1	408 (82)b,A	431 (68)b,A	452 (83)b,c,A	465 (75)b,c,A
	Av-2	454 (89)b,A	451 (80)b,A	469 (107)c,A	515 (79)c,A
DO (mg/L)	Ykr-1	11.4 (0.6)a,C	10.6 (0.9)b,B	9.0 (0.4)c,A	10.1 (0.8)b,B
	Ykr-2	11.4 (1.2)a,C	9.9 (1.5)a,b,B	7.8 (0.6)a,A	9.1 (1.3)a,b,B
	Av-1	11.1 (0.6)a,C	10.0 (0.8)a,b,B	8.4 (0.6)b,A	9.8 (1.0)a,b,B
	Av-2	11.1 (1.1)a,C	9.5 (1.2)a,B	7.6 (0.7)a,A	8.9 (1.5)a,B
TN (mg/L)	Ykr-1	1.3 (0.9)a,A	2.4 (2.8)a,A	1.2 (0.8)a,A	1.0 (1.3)a,A
	Ykr-2	2.5 (1.9)b,A	3.3 (3.6)a,A	2.0 (1.3)a,b,A	1.4 (0.7)a,A
	Av-1	3.6 (1.4)b,c,A	3.6 (2.2)a,A	3.3 (2.2)b,c,A	2.7 (2.5)a,A
	Av-2	4.2 (1.2)c,A	3.9 (2.5)a,A	4.2 (1.6)c,A	5.4 (2.6)b,A
NO <sub>2</sub> (mg/L)	Ykr-1	0.02 (0.04)a,A	0.03 (0.06)a,A,B	0.09 (0.11)a,B	0.03 (0.07)a,A,B
	Ykr-2	0.07 (0.09)a,b,A	0.18 (0.13)a,A	0.14 (0.13)a,A	0.12 (0.18)a,A
	Av-1	0.04 (0.11)a,A	0.11 (0.08)a,A	0.40 (0.85)a,A	0.08 (0.17)a,A
	Av-2	0.15 (0.17)b,A	0.39 (0.41)b,A	1.09 (1.10)b,B	1.04 (0.67)b,B
NO <sub>3</sub> (mg/L)	Ykr-1	3.1 (2.7)a,A	3.5 (2.3)a,A	2.8 (1.9)a,A	3.0 (3.6)a,A
	Ykr-2	4.8 (2.8)a,A	4.3 (2.9)a,A	3.6 (2.0)a,A	4.4 (4.0)a,b,A
	Av-1	10.4 (6.3)b,A	9.8 (6.4)b,A	9.8 (5.5)b,A	9.5 (7.5)b,c,A
	Av-2	11.6 (4.4)b,A	9.6 (5.8)b,A	10.0 (6.0)b,A	10.7 (8.5)c,A
SO <sub>4</sub> (mg/L)	Ykr-1	14.9 (4.9)a,A	14.1 (4.0)a,A	13.7 (4.3)a,A	15.8 (2.6)a,A
	Ykr-2	17.3 (6.5)a,A	18.8 (4.5)b,A	15.0 (2.9)a,A	18.3 (3.2)a,A
	Av-1	21.1 (8.6)a,A	21.0 (4.8)b,A	23.1 (6.1)b,A,B	27.2 (4.2)b,B
	Av-2	21.3 (8.4)a,A	21.1 (3.5)b,A	20.0 (6.4)b,A	27.0 (3.3)b,B
PO <sub>4</sub> (mg/L)	Ykr-1	0.11 (0.08)a,A	0.08 (0.03)a,A	0.30 (0.23)a,B	0.23 (0.15)a,B
	Ykr-2	0.26 (0.23)b,A	0.29 (0.22)b,A	0.23 (0.18)a,A	0.38 (0.23)a,A
	Av-1	0.12 (0.10)a,A	0.12 (0.07)a,A	0.26 (0.25)a,B	0.23 (0.11)a ,A,B
	Av-2	0.37 (0.21)b,A	0.55 (0.20)c,A	0.54 (0.29)b,A	0.76 (0.18)b,B
NH <sub>4</sub> (mg/L)	Ykr-1	0 (0)a,A	0.13 (0.29)a,A	0.19 (0.41)a,A	0.01 (0.01)a,A
	Ykr-2	0.34 (0.49)a,A	1.14 (1.37)b,B	0.45 (0.62)a,A,B	0.69 (0.39)a,A,B
	Av-1	0.03 (0.09)a,A	0.20 (0.26)a,A	1.17 (3.03)a,A	0.16 (0.25)a,A
	Av-2	0.88 (0.95)b,A	2.65 (1.59)c,A,B	3.53 (3.22)b,B,C	5.27 (4.44)b, C

Note: Means with the same lowercase letters in each column are not significantly different ( $p > .05$ ).  
 Means with the same uppercase letters in each row are not significantly different ( $p > .05$ ).  
 The standard deviation is shown in parentheses.

in the water was an important factor contributing to the reduction of pH at the sampling points.

### Electrical Conductivity (EC)

The highest monthly average EC (567 µS/cm) was measured in Av-2 and the lowest (97 µS/cm) in Ykr-1. According to the SWQR, in terms of EC, the water quality was first class at Ykr-1 and second class at the other sampling points.

Of all the measured averages, Ykr-1 had the lowest EC and Av-2 had the highest. Although the EC in hazelnut plantation-dominated Av-1 was higher than that of the forest-dominated Ykr-1, the EC of Ykr-2 was higher than that of Ykr-1, and the EC of Av-2 was higher than in Av-1. In other words, the EC increased in the sampling points representing the settlement areas of both watersheds (Table 2). This rise may have resulted from the intense human influence in the agricultural and residential areas. Similarly, Liu et al. (2009) found a strong positive correlation between EC and settlement and

agricultural lands and a high negative correlation between EC and forestlands. Chow et al. (2011) determined that in watersheds with different proportions of agricultural land, as the agricultural area increased, the EC also increased. It has been emphasized in many other studies that the EC is higher in agriculture-, settlement-, or grassland-dominated watersheds than in forest-dominated watersheds (Ahearn et al., 2005; Haidary et al., 2013; Shilla & Shilla, 2011; Wang et al., 2013).

The EC was lowest at Ykr-1 for all seasons. In the winter and spring, the EC values were similar for all points except Ykr-1, whereas Av-2 had a higher value in the summer and autumn. In addition, there was a continued increase in the EC of Ykr-1 from winter to autumn (Table 3). It is thought that this situation was a result of the increased ion concentration in the summer and autumn seasons due to the lower streamflow rate in Ykr-1 compared to Av-1. Indeed, in a study investigating the effects of land use on water and soil properties, it was observed that the EC increased at low flow rates and decreased at high flow rates (Usta, 2011).

### Dissolved Oxygen (DO)

The highest monthly average DO (12.8 mg/L) was measured in Ykr-1 and the lowest (6.9 mg/L) in Av-2. Because the average DO of the points exceeded 8 mg/L, the water quality at all sampling points was rated as first class according to the SWQR.

According to all measurement averages, the DO of Ykr-1 was higher than at the other sampling points (Table 2). This finding demonstrated that water pollutants had increased in the agricultural and settlement areas. Similar studies have found a negative relationship between DO and the proportion of urban areas in watersheds (Haidary et al., 2013), although a positive relationship has been found with the proportion of forest areas (Tu, 2013). In a study examining the water quality of lakes surrounded by urban and rural areas, a lower DO was found in the lake surrounded by urban areas (Merugu & Seetharaman, 2013).

No difference was found between the sampling points except in winter. In the other seasons, Ykr-1 had the highest DO, which decreased significantly in the sampling points representing the settlement areas (Table 3). Especially in summer, this DO decrease may have been due to the rise in water temperature and the reduced rainfall. In a similar study, it was stated that the decrease in the DO during the dry season may have been due to the pollution introduced as an effect of urbanization, and the DO increase in the rainy season may have been caused by the presence of the clean water intake (Merugu & Seetharaman, 2013). The most important reason for the lowest values in summer and the highest values in winter at all points was the change in the water temperature.

### Total Nitrogen (TN)

The highest monthly average TN (8.6 mg/L) was measured in Av-2 and the lowest (0.1 mg/L) in Ykr-1. The TN averages of all points except Av-2 were below 3.5 mg/L, and therefore, their water quality was rated as first class according to the SWQR, while the water quality of Av-2 was rated as second class.

According to all measurement averages, the TN of Av-1 was found to be higher than that of Ykr-1. Although the TN of Ykr-1 and Ykr-2 were similar, the TN of Av-2 was higher than that of Av-1 (Table 2). In general, the amount of TN in the agriculture-dominated watershed was higher than in the forest-dominated watershed, i.e., fertilizer usage and the human effect increased the TN in the water. In a number of studies, a higher TN was found in agriculture-dominated watersheds than in forest-dominated watersheds (Ahearn et al., 2005; Kim et al., 2007; Wang et al., 2009). In a similar study, a positive relationship was found between TN

and the proportion of urban and agricultural land in the watersheds, whereas a negative relationship was found between TN and the proportion of forest areas (Haidary et al., 2013; Tu, 2013). As a result of the measurements at 12 different points of a river in China, it was found that the TN concentration had increased significantly from the forest-dominated sampling points to the agriculture- and settlement-dominated sampling points (Wang et al., 2013).

The TN values of the sampling points did not change seasonally. The TN of Ykr-1 was lower than in Av-1 in the winter and summer seasons, whereas an increase was detected in the sampling points representing the settlement areas (Ykr-2 and Av-2) (Table 3). No statistical difference was found between the sampling points in the spring because the TN in Ykr-1 and Ykr-2 were higher than in the other seasons. In the spring, parallel to the increase in temperature and rainfall, the nitrogen became free due to the decomposition of organic matter and humus in the forest areas and may have been washed away by the rainfall. Several studies reported that soil moisture and temperature were two important factors affecting the microbial activity and nitrogen mineralization, and they determined that the mineralization rate in the soil increased with increasing temperature (Butler et al., 2012; Trammell et al., 2017).

### Nitrite (NO<sub>2</sub><sup>-</sup>)

The highest monthly average NO<sub>2</sub><sup>-</sup> (3.4 mg/L) was measured in Av-2, and the lowest (0.0 mg/L) was measured at all points at different periods. Of all measurement averages, only the NO<sub>2</sub><sup>-</sup> of Av-2 was higher than the values at the other sampling points, and these were similar (Table 2). This situation was thought to have been caused by the mixing of domestic and animal waste in the water along with the effect of the high population of Avlayan village and the proximity of the settlement areas to the stream, in addition to a certain amount of nitrite from the agriculture-dominated watershed. Accordingly, it can be said that the settlement areas had a great effect on NO<sub>2</sub><sup>-</sup>. In a study conducted in 24 sub-watersheds in Japan, a significant positive relationship was found between the proportion of urban areas in the watersheds and NO<sub>2</sub><sup>-</sup> (Haidary et al., 2013). In a similar study, a significant positive relationship was found between the proportion of urban areas and the total amount of nitrite and nitrate-nitrogen, whereas a significant negative relationship was found with the proportion of forest areas (Tu, 2013).

The NO<sub>2</sub><sup>-</sup> value of Av-2 was higher than other sampling points for all seasons and increased at this point in summer and autumn (Table 3).

### Nitrate (NO<sub>3</sub><sup>-</sup>)

The highest monthly average NO<sub>3</sub><sup>-</sup> (24.7 mg/L) was measured in Av-2 and the lowest (0.3 mg/L) in Ykr-1. The average NO<sub>3</sub><sup>-</sup>-N (nitrate-nitrogen) values of Ykr-1, Ykr-2, Av-1, and Av-2 were 0.67 mg/L, 0.95 mg/L, 2.19 mg/L, and 2.31 mg/L, respectively. The average NO<sub>3</sub><sup>-</sup>-N values of all sampling points were below 3 mg/L, and thus, according to the SWQR, their water quality was rated as first class.

According to all measurements and seasonal averages, the amount of NO<sub>3</sub><sup>-</sup> of Av-1 was about three times higher than that of Ykr-1 (Tables 2 and 3). This result shows that the agricultural lands had a positive impact on NO<sub>3</sub><sup>-</sup>, whereas the forest areas had a negative impact on NO<sub>3</sub><sup>-</sup> as highlighted in other studies (Lee et al., 2010; Miller et al., 2011). In the studies conducted in different watersheds comprised of agriculture-dominated and forest-dominated lands, the NO<sub>3</sub><sup>-</sup>-N of the agricultural watershed was found to be higher than in the forested watershed (Brisbois et al., 2008; Wang et al., 2013). The reason was that the increase in the amount of NO<sub>3</sub><sup>-</sup> concentration in the water due to the use of fertilizers in agricultural lands (Ahearn et al., 2005; Chow et al., 2011;

Coulter et al., 2004; Kim et al., 2007). However, the settlement areas did not have a significant effect on the amount of  $\text{NO}_3^-$ . In other words, no significant change was observed in the  $\text{NO}_3^-$  of the sampling points after the settlement areas.

The  $\text{NO}_3^-$  values of Av-1 and Av-2 were higher than Ykr-1 and Ykr-2 for all seasons. In terms of the sampling points, the nitrate did not change seasonally (Table 3).

#### Sulfate ( $\text{SO}_4^{2-}$ )

The highest monthly average  $\text{SO}_4^{2-}$  (31.4 mg/L) was measured in Av-1, and the lowest was (6.4 mg/L) in Ykr-1. According to all measurement averages, the  $\text{SO}_4^{2-}$  of Av-1 was found to be higher than that of Ykr-1. Although the  $\text{SO}_4^{2-}$  of Av-2 was similar to that of Av-1, the  $\text{SO}_4^{2-}$  of Ykr-2 was higher than that of Ykr-1 (Table 2). This finding indicates that the agricultural and settlement areas had a positive effect on  $\text{SO}_4^{2-}$  concentration. In a study conducted in the USA, a strong positive correlation was found between  $\text{SO}_4^{2-}$  and urban and agricultural land, and a high negative correlation between  $\text{SO}_4^{2-}$  and forest lands (Liu et al., 2009).

In the high rainfall season, the  $\text{SO}_4^{2-}$  values of all sampling points were found to be similar. This may have been due to the dilutive effect of the rainfall. In other seasons, the average  $\text{SO}_4^{2-}$  of Av-1 was higher than that of Ykr-1, while the  $\text{SO}_4^{2-}$  of Av-1 and Av-2 was similar. Only in the spring season, Ykr-2 has a higher value than Ykr-1 (Table 3). As a result, seasonal evaluations demonstrated that the  $\text{SO}_4^{2-}$  was high in agricultural and settlement areas where human impact is great.

The  $\text{SO}_4^{2-}$  did not change seasonally in Ykr-1 or Ykr-2; however, an increase was seen in Av-1 in summer and autumn and Av-2 in autumn (Table 3). This may have been due to the increase in  $\text{SO}_4^{2-}$  concentration in the water because of the ammonium sulfate fertilizer applied to the hazelnut plantations at the end of May in conjunction with the increasing rainfall in the autumn.

#### Phosphate ( $\text{PO}_4^{3-}$ )

The highest average monthly  $\text{PO}_4^{3-}$  (1.1 mg/L) was measured in Av-2, while the lowest (0.0 mg/L) was measured in all sampling points at different periods. The average TP (total phosphorus) for the sampling points was calculated from the  $\text{PO}_4^{3-}$  concentrations. The average TP of Ykr-1, Ykr-2, Av-1, and Av-2 were 0.06 mg/L, 0.09 mg/L, 0.06 mg/L, and 0.18 mg/L, respectively. The values were seen to increase in the sampling points representing the settlement areas. According to the SWQR, the water quality of Ykr-1 and Av-1 was rated as first class in terms of TP, while that of Ykr-2 and Av-2 was rated as second class.

When all measurement averages were considered, the  $\text{PO}_4^{3-}$  of Ykr-1 and Av-1 were similar. There was a significant increase at the sampling points Ykr-2 and Av-2 located in the settlement areas, with Av-2 exhibiting the highest  $\text{PO}_4^{3-}$  (Table 2). Domestic waste and detergents were the reasons for the increase in the  $\text{PO}_4^{3-}$  in the settlement areas. This value may have increased more in Av-2 because of the higher population of Avlayan village. In a study conducted in the USA, a significant positive relationship was found between phosphorus and urban and agricultural areas in the watersheds (Liu et al., 2009), although in another study, a significant positive relationship was found between phosphorus and urban areas alone (Tu, 2013). In both studies, a significant negative relationship was found between phosphorus and forest areas. In a study conducted on different representative land use, the  $\text{PO}_4^{3-}$  of watercourses characterized by urban areas was found to be higher than in those characterized by bushland (Shilla & Shilla, 2011). In a study investigating the water quality of lakes surrounded by urban

areas and rural areas, the  $\text{PO}_4^{3-}$  of the lake surrounded by rural areas was found to be lower than that of the lake surrounded by urban areas (Merugu & Seetharaman, 2013).

It was determined that the  $\text{PO}_4^{3-}$  of Ykr-1 and Av-1 was similar in all seasons and that Av-2 had a higher value than Av-1. In winter and spring, Ykr-2 had a higher value than Ykr-1. In general, in summer and autumn, the  $\text{PO}_4^{3-}$  at all sampling points increased compared to the other seasons (Table 3). This can be attributed to the leaching of phosphorus as an effect of the heavy rainfall in the summer and autumn seasons. In a similar study, a significant positive relationship was found between urban areas and total phosphorus in the water, and it was reported that the total phosphorus increased in summer and after heavy rainfall (Rothenberger et al., 2009). In a study in China, the total phosphorus concentration of sub-watersheds with settlement-dominated areas was found to be very high during the rainy season (Wang et al., 2009). In another study, it was reported that the high  $\text{PO}_4^{3-}$  of a lake surrounded by an urban area may have been caused by the heavy flow and leaching in the settlement areas during the monsoon season (Merugu & Seetharaman, 2013). In a similar study in Zimbabwe, a strong positive relationship was found between settlement areas and TP in both rainy and dry seasons, and between agricultural lands and TP in the rainy season (Kibena, 2014).

#### Ammonium ( $\text{NH}_4^+$ )

The highest monthly average  $\text{NH}_4^+$  (12.7 mg/L) was measured in Av-2, and the lowest (0.0 mg/L) was measured in all points at different periods. The average  $\text{NH}_4\text{-N}$  (ammonium nitrogen) of Ykr-1, Ykr-2, Av-1, and Av-2 were, respectively, 0.06 mg/L, 0.52 mg/L, 0.29 mg/L, and 2.46 mg/L. The average  $\text{NH}_4\text{-N}$  of Ykr-1 was below 0.2 mg/L, and therefore, according to SWQR, its water quality was rated as first class. Since the Ykr-2 and Av-1 values were between 0.2 and 1 mg/L, their water quality was rated as second class, and because the value of Av-2 exceeded 2 mg/L, its water quality was rated as fourth class.

According to all measurement averages, the  $\text{NH}_4^+$  of Ykr-1, Ykr-2, and Av-1 were found to be similar, whereas the  $\text{NH}_4^+$  of Av-2 was significantly higher than in these points (Table 2). It is thought that the high amount of ammonium in Av-2 was caused by the wastewater from the settlement areas and barns close to the stream mixing with the water. In a similar study, the  $\text{NH}_4^+$  concentrations of stream points representative of urban land use were found to be higher than those characterized by agricultural and forest areas (Knee & Encalada, 2014). Again, as a result of the measurements at 12 different points of a river in China, it was determined that the  $\text{NH}_4\text{-N}$  concentration had increased significantly from the forest-dominated sampling points to the agriculture- and settlement-dominated sampling points (Wang et al., 2013).

The highest ammonium was seen in Av-2 in all seasons. At other points, in seasons other than spring, the amount of ammonium was similar, whereas in Ykr-2, an increase occurred in the spring (Table 3). No seasonal change was observed in the  $\text{NH}_4^+$  of the Ykr-1 or Av-1 points. Although the  $\text{NH}_4^+$  of the Ykr-2 and Av-2 points was low in winter, it increased in the other seasons (Table 3). This may have been the result of the frequent use of animal waste as fertilizer during these seasons.

### Conclusion and Recommendation

Water quality is very important for Big Melen Stream in terms of human health, as it meets the water needs of nearly half of the population of Istanbul, Turkey's most populous city. Accordingly, this study evaluated the water quality of the Avlayan and Yukarıkaraköy creek watersheds,

which form the sub-watersheds of the Big Melen watershed. The stream water of Ykr-1 was of high quality in terms of all parameters measured and rated as very good according to the criteria specified in the Turkish Surface Water Quality Regulations. Point Av-1, because of its high EC and  $\text{NH}_4^+$ , and Ykr-2, due to its high TP value in addition to these parameters, both had a good water status with slight pollution. Point Av-2 exhibited a highly polluted and poor water status because of its very high  $\text{NH}_4\text{-N}$ . In other words, the quality of the water coming from the forest-dominated watershed was higher than the water coming from the watershed where the hazelnut plantations are located. However, when the watershed water passed from the forestlands to the settlements and from the hazelnut plantations to the settlements, the concentrations of some pollutants increased and the water quality deteriorated.

Accordingly, it may be recommended that settlement areas should be limited in the coastal protection band of the Big Melen Stream that supplies water to the city of Istanbul. In addition, it may be recommended that the small watersheds supplying water to the Big Melen watershed should be afforested as much as possible. Moreover, the banks along the streams in the watersheds should be afforested for a certain distance in order to contain the pollutants by creating a buffer against them.

The results of this study characterized two small watersheds feeding the Big Melen Stream. Starting from the threshold of the plain opening from the forest, all mountainous areas of the Big Melen watershed contain hazelnut plantations. Therefore, this study is capable of representing all these areas of the watershed. However, better results can be obtained by examining the relations between the measurements made by government agencies at various points of the watercourse and the land use representing these points.

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