MAS JAPS 7(Özel Sayı): 1121–1133, 2022

MAS Journal of Applied Sciences
Uygulamalı Bilimler Dergisi
ISSN: 2757-5675
masjaps.com

DOI: http://dx.doi.org/10.5281/zenodo.7451699

Araştırma Makalesi / Research Article

Investigation of The Possibilities of Using The Wastewater of Kırklareli Region in Agriculture

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Geliş Tarihi (Received): 01.11.2022 **Kabul Tarihi (Accepted)**: 30.11.2022

Abstract

Water is a vital resource for the survival of all living things. In recent years, rapid population growth and the increase in industrial, urban and agricultural practices cause pollution and depletion of water resources. For this reason, it is very important to protect existing water resources and reuse waste water. In this study, it was aimed to investigate the effects of some heavy metal parameters on the water quality of the wastewater of the stations determined in Kırklareli Stream and to reuse the wastewater in agriculture. Within this scope, 10 different stations were determined by considering the various characteristics of the stations selected on the Kırklareli Stream. Seasonal water samples were taken from each station between February and October 2018. Heavy metal analyzes were performed with an inductively coupled plasma-optical emission spectroscopy (ICP-OES) device. The results obtained from the study were determined according to the Classes of Inland Surface Water Resources (CPCB) in the Water Pollution Control Regulation. According to this; Differently from other heavy metal parameters, the mercury (Hg) parameter of Kırklareli stream water samples is seasonal and station-based. class, Lead (Pb) and Manganese (Mn) II. determined to be of class quality. Analysis of variance, one-way analysis of variance (ANOVA) and correlation analysis were performed in a repeated measurement experiment on the measurement values of water samples. Significant differences and relationships between parameters were determined statistically.

Keywords: Wastewater, domestic waste, industrial waste, water quality. water pollution, reuse

INTRODUCTION

Water is essential basic sources of life for the continuity of life of all living things. The world population is expected to be 9.3 billion in 2050 (Özbay and Kavaklı, 2008). Recently, the demand for food and water has been increasing due to the population growth. The quality and quantity of water resources are decreasing day by day due to reasons such as rapid population growth, urbanization, economic growth targets, intense agricultural activities and increasing pollution pressure on water resources as a result of industrialization, and climate change. The total amount of water in the world is 1 billion 400 million km^3 (1 km^3 = 1 billion m^3) and 97.5% of this water consists salt water in the seas and oceans. It has been determined that 2.5% of total water is fresh which can be used for various purposes (Ulusoy, 2007). Contrary to the general perception, Türkiye is not a richest country in terms of freshwater resources. Yearly usable water per capita is over 10000 cubic meters in water-rich countries. This is 1346 m^3 per capita in Türkiye (DSİ, 2020). By the year 2030 this amount will decline to 1,000 m^3 per capita/year with an expected population of 100 million. These predictions show that Türkiye will be place the water-poor countries. European Environment Agency pointed out that by the year 2030 increasing levels of water deficit may be experienced in many regions of Turkey (European Environment Agency (EEA), 2005, Saraoğlu, 2014). For this reason, the protection and efficient management of existing water resources is crucial in terms of ensure the recycling and reuse of the used part of water. In the studies on reuse of waste water and its usage areas, the guidelines published by the European Union Directives, the United Nations Environment Program and the Environmental Protection Agencies, covering the issues such as reuse of waste water, treatment, interested area of use, potentials, risks and precautions (Asan 2013, Demir et al.,2017). The use of recycled wastewater as irrigation water in Turkey is evaluated according to the Wastewater Treatment Plants Technical Procedures Notification No. 27527 published in the Official Paper dated 20 March 2010. Quality criteria and technical limitations for treated wastewater to be used for agricultural purposes in Turkey are defined by the Water Pollution Control Regulation Technical Procedures Notification (Official Paper, 2004) (Gülocak, 2019). According to the studies; approximately 70% of the water resources is used for irrigation in the world. For this reason, the use of treated wastewater imported in order to pay attention to water consumption and to support the decreasing water resources and to use it in irrigation. (Madera-Parra, C.A. et al. 2015; Aşik and Özsoy, 2016, Bingül and Altıkat, 2017). In addition, treated wastewater is reused in many areas for urban, industrial, environmental and recreation, groundwater feeding, agricultural activities and increase of drinkable water resources. This study aims to evaluate quality of the water coming out of the domestic-industrial wastewater treatment plants located on the Kırklareli stream route and discharged to the stream Management" in terms of agricultural purposes.

MATERIAL and METHOD

Place of research area, collecting water samples and analysis method

Kırklareli Province, located in the Thrace region of the Marmara Region, is a border province established on the Ergene plain and Yıldız Mountains.

It is located in the west of Edirne, in the north of Bulgaria, in the northeast of the Black Sea, and in the south and southeast of Tekirdağ (Figure 1).

Figure 1. The location of Kırklareli province on the map of Turkey

The study aimed at 10 sample stations considering the human use on Kırklareli stream, water treatment facilities along the stream, textile factory, dairy farms, improvement works, proximity to the main road, crops planted in agricultural lands and fertilizers consumed in agriculture. These stations are shown in Table 1.

Table 1. The stations from which the samples were taken

No	The Name of the Place from Which the Sample Is Taken	Coordinates	
		Latitude	Longitude
1	Before Kırklareli Central Waste Water Treatment Plant	N 41°41.8347'	E 027°12.6233'
2	After Kırklareli Central Waste Water Treatment Plant	N 41°41.7740'	E 027°12.5566'
3	Before a textile factory by the creek	N 41°41.0837'	E 027°12.1068'
4	After a textile factory by the creek	N 41°41.0675'	E 027°12.1028'
5	Next to the Kırklareli-Istanbul main road passing over the creek	N 41°40.9578'	E 027°11.8447'
6	Before Kırklareli/ Kavaklı Town settlement area	N 41°39.3487'	E 027°10.1491'
7	After Kırklareli/Kavaklı Town settlement area	N 41°39.0874'	E 027°09.9495'
8	Kavaklı Town, after several dairy facilities	N 41°39.6126'	E 027°10.3270'
9	Before Kırklareli/Kavaklı Partial Sewage and Wastewater Treatment Plant	N 41°38.7703'	E 027°09.8446'
10	After Kırklareli/Kavaklı Partial Sewage and Wastewater Treatment Plant	N 41°38.7616'	E 027°09.8219'

Samples collected once seasonally in 2018. Sample values were used in February for the winter season, March-April-May for the spring season, June-July for the summer season, and October for the autumn season. The representation of the determined stations on the map is given in Figure 2.

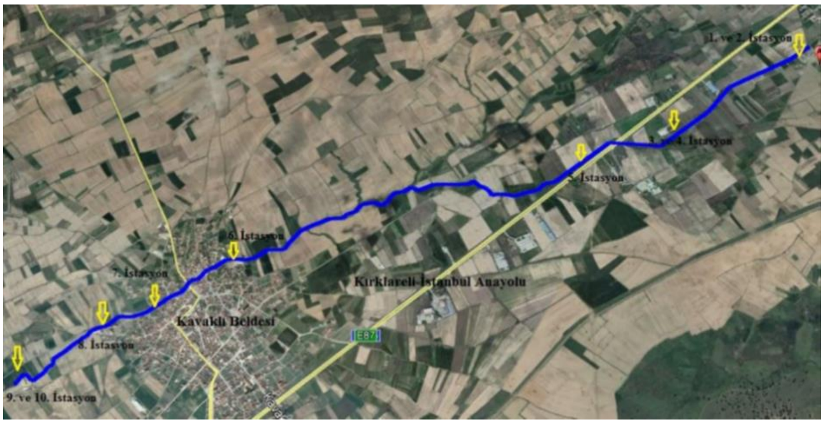


Figure 2. The representation of the stations determined on the Kırklareli creek on the map (Gülocak, 2019)

Analysis of water samples was carried out in the laboratory of Atatürk Soil, Water and Agricultural Meteorology Research Institute with (ICP-OES) and (HGAAS), water analysis parameters and analysis methods are given in Table 2. The results obtained by laboratory tests from water samples were evaluated according to the Classes of Inland Surface Water Resources in the Water Pollution Control Regulation. Heavy metal limit values for valuation of water resources analysis results in terms of irrigation water quality are given Table 3 (Official Gazette, 13.02.2008, issue: 26786).

Table 2. Water analysis parameters and analysis methods (Gülocak, 2019)

Parameters	Analysis Methods
Aluminum (Al)	ICP-OES (inductively coupled plasma-optical emission spectrometry)
Copper (Cu)	
Boron (B)	
Cadmium (Ca)	
Zinc (Zn)	
Iron (Fe)	
Tin (Sec)	
Cobalt (Co)	
Chromium (Cr)	
Lead (Pb)	
Sulfur (S)	
Magnesium (Mg)	
Manganese (Mn)	
Potassium (K)	
Sodium (Na)	
Nickel (Ni)	
Phosphorus (P)	
Titanium (Ti)	
Vanadium (V)	
Mercury (Hg)	(HGAAS) In hydride-forming atomic absorption spectrometry
Arsenic (Ace)	
Antimony (Sb)	
Selenium (Se)	

Table 3. Quality criteria according to the classes of inland water resources (Official Gazette, 13.02.2008, issue: 26786)

WATER QUALITY PARAMETERS	WATER QUALITY CLASSES			
	I	II	III	IV
C) Inorganic contamination parameters[d]				
1) Mercury (μg Hg/L)	0.1	0.5	2	> 2
2) Cadmium (μg Cd/L)	3	5	10	> 10
3) Lead (μg Pb/L)	10	20	50	> 50
4) Arsenic (μg As/L)	20	50	100	> 100
5) Copper (μg Cu/L)	20	50	200	> 200
6) Chromium (total) (μg Cr/L)	20	50	200	> 200
7) Chromium (μg Cr+6/L)	immeasurably small	20	50	> 50
8) Cobalt (μg Co/L)	10	20	200	> 200
9) Nickel (μg Ni/L)	20	50	200	> 200
10) Zinc (μg Zn/L)	200	500	2000	> 2000
11) Cyanide (total) (μg CN/L)	10	50	100	> 100
12) Fluoride (μg F^-/L)	1000	1500	2000	> 2000
13) Free chlorine (μg Cl2/L)	10	10	50	> 50
14) Sulfur (μg S=/L)	2	2	10	> 10
15) Iron (μg Fe/L)	300	1000	5000	> 5000
16) Manganese (μg Mn/L)	100	500	3000	> 3000
17) Boron (μg B/L)	1000[e]	1000[e]	1000[e]	> 1000
18) Selenium (μg Se/L)	10	10	20	> 20
19) Barium (μg Ba/L)	1000	2000	2000	> 2000
20) Aluminum (mg Al/L)	0.3	0.3	1	> 1

Statistical Evaluation of Data

Analyzes were performed using the SPSS 23.0 statistical package program. Correlation between parameters was evaluated with Pearson correlation coefficient. Type 1 error level was determined as 0.05 in the analyzes. Normality assumption for analyzes with Kolmogorov-Smirnov and Shapiro Wilk tests; The homogeneity of the variances was examined with the Levene test. In cases where the assumption of normality was not provided, the data were subjected to logarithmic transformation, Within the scope of one-way analysis of variance, Tukey's multiple comparison test was used to determine from which groups the statistically significant differences originated. Whether the assumption of sphericity was met in the analyzes was analyzed with the Mauchly test. Greenhouse and Geisser and Huynh and Feldt corrections were used in cases where the sphericity assumption was not met. (Gülocak, 2019).

FINDINGS AND DISCUSSION

The classification of Quality Criteria by Classes of Inland Surface Water Resources for seasonal heavy metal parameters of Kırklareli Stream water samples is shown in Table 4.

Table 3. Classification of water samples according to CPCB for seasonally heavy metal parameters (Gülocak, 2019)

Parameters	**Seasons**				**CPCB**
	Winter	**Spring**	**Summer**	**Autumn**	
Lead (Pb)(µg/L)	15.52	5.24	2.49	5.68	II
Copper (Cu)(µg/L)	0	0.09	0	0.25	I
Zinc (Zn)(µg/L)	0.92	3.29	0.49	5.51	I
Chromium (Cr)(µg/L)	0.03	0.9	0	0.01	I
Iron (Fe)(µg/L)	106.73	25.94	5.95	31.38	I
Manganese (Mn)(µg/L)	72.24	82.54	19.24	188.36	II
Cobalt (Co)(µg/L)	0.02	0.09	0.01	0.01	I
Nickel (Ni)(µg/L)	0.12	0.22	0	0.68	I
Boron (B)(µg/L)	112.2	165.8	79.93	122.66	I
Tin (Sn)(µg/L)	5.6	5.4	1.96	2.27	
Aluminum (Al)(µg/L)	62.56	6.41	3.58	6.81	I
Cadmium (Cd)(µg/L)	0	0	0	0.01	I
Sulfur (S)(mg/L)	19.86	24.64	15.8	57.42	
Vanadium (V)(µg/L)	3.55	2.19	1.63	2.24	
Titanium (Ti)(µg/L)	9.69	3.46	0.1	3.8	
Mercury (Hg)(µg/L)	0	0.41	0	0.97	III
Arsenic (As)(µg/L)	3.09	4.89	1.85	4.27	I
Selenium (Se)(µg/L)	0.43	0.27	1.27	0.68	I
Antimony (Sb)(µg/L)	0.93	1.16	0.01	0.41	

Class I 🟦 Class II 🟩 Class III 🟥 Class IV

Parameter of Pb is determined as I.class quality in spring, summer and autumn seasons and II.class in winter season. Mn parameter detected I.class in winter, spring and summer season and II. Class in autumn season. While Hg parameter is determined as I class in winter and summer season quality of Hg found as II class in spring and III. Class in autumn seasons. Cu, Zn, Cr, Fe, Co, Ni, B, Al, Cd, As, Se parameters are dedected as I.class in all seasons. The classification of the Quality Criteria by Classes of Inland Surface Water Resources for the heavy metal parameters of Kırklareli Stream water samples on the basis of stations is shown in Table 5.

Table 4. Classification of water samples according to CPCB for heavy metal parameters on the basis of stations (Gülocak, 2019)

Parameters	**Stations**										**CPCB**
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
Lead (Pb)(µg/L)	10,05	1,56	4,42	4,26	6,34	8,32	8,22	10,48	3,8	3,3	II
Copper (Cu)(µg/L)	0,73	0	0	0	0	0	0	0	0	0	I
Zinc (Zn)(µg/L)	8,87	4,27	1,88	1,95	1,65	1,27	0,21	4,88	0,4	0	I
Chromium (Cr)(µg/L)	3,93	0	0	0	0	0	0	0	0	0	I
Iron (Fe)(µg/L)	55,61	7,35	17,31	18,63	35,93	50,05	48,93	61,4	18,44	18,03	I
Manganese (Mn)(µg/L)	89,12	62,34	90,58	65,3	81,59	88,73	91,82	107	57,61	74,79	II
Cobalt (Co)(µg/L)	0,4	0	0	0	0,02	0,01	0	0	0,01	0,03	I
Nickel (Ni)(µg/L)	1,15	0,21	0,08	0	0,11	0,05	0,1	0,16	0,13	0,14	I
Boron (B)(µg/L)	324,8	160,7	115,4	115	108,8	86,94	85,47	87,56	93,25	107,5	I
Tin (Sn)(µg/L)	9,56	2,92	4,83	5,33	3,52	2,08	2,7	3,15	3,73	2,92	
Aluminum (Al)(µg/L)	10,57	4,89	6,57	6,89	18,86	26,14	25,68	18,69	7,37	14,29	I
Cadmium (Cd)(µg/L)	0	0	0	0	0	0	0	0	0	0,01	I
Sulfur (S)(mg/L)	28,8	31,23	21,55	19,43	20,31	19,28	19,53	21,26	43,98	46,27	
Vanadium (V)(µg/L)	1,11	1,25	1,13	1,27	1,13	1,83	1,91	1,75	5,09	5,91	
Titanium (Ti)(µg/L)	17,95	0,15	0,31	0,05	2,94	4,1	4,02	2,92	0,31	2,04	
Mercury (Hg)(µg/L)	0,26	0,06	0,63	0,76	0,21	0,21	0,53	0,16	0,31	0,07	III
Arsenic (As)(µg/L)	3,9	3	3,04	3,59	3,55	2,93	3,04	2,97	5,87	6,32	I
Selenium (Se)(µg/L)	0,73	0,51	0,54	0,53	0,64	0,6	0,68	0,67	0,61	0,53	I
Antimony (Sb)(µg/L)	0,82	0,79	0,59	0,81	0,64	0,65	0,67	0,67	0,77	0,83	

Class I 🟦 Class II 🟩 Class III 🟥 Class IV

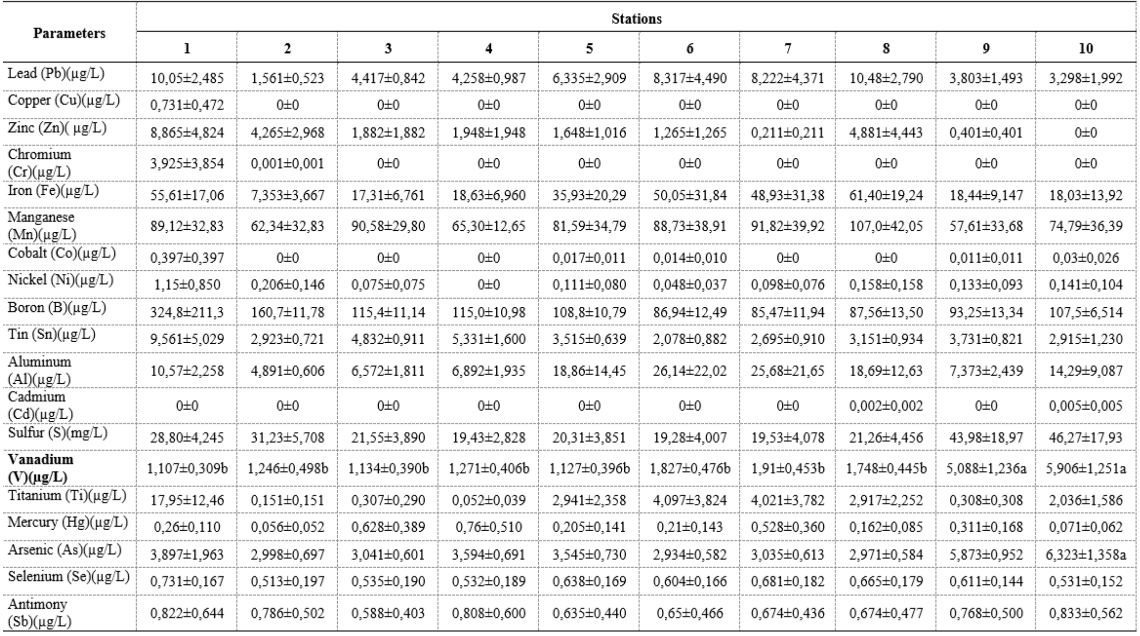
While Pb parameter is determined as II.class in 1.and 8. stations, it is find out that I.class in other stations. Mn parameter determined as II.class in 8. station and I.class in all other stations. Hg parameter is determined as I class quality in 2-10. station and II.class in 1-5-6-8-9 and also III.class in the stations 3-4-7. All other parameters determined as first class in all stations. Table 6 shows, the results of the analysis of variance for the heavy metal parameters of the water samples in the repeated measurement treatment order on a seasonal basis. It was investigated whether there is a statistically significant difference between the seasonal averages for the heavy metal parameters of the water samples. There is a statistically significant difference between the averages of at least two seasons in terms of Pb, Fe, Mn, Ni, Sn, Al, S and As parameters (p<0,05). Differences for Pb, Fe, Sn parameters from winter season and difference between the averages of manganese, nickel, sulfur and arsenic parameters is due to the autumn season.

Table 5. The results of the variance analysis for the heavy metal parameters of water samples in a trial scheme with repeated measurements on a seasonal basis (Gülocak, 2019)

Parameters	**Seasons**			
	Winter	**Spring**	**Summer**	**Autumn**
Lead (Pb)(μg/L)	15,517±3,8348a	5,238±1,0885b	2,493±0,6317b	5,678±1,2660b
Copper (Cu)(μg/L)	0±0	0,087±0,087	0±0	0,251±0,251
Zinc (Zn)(μg/L)	0,916±0,6261	3,285±1,1277	0,493±0,493	5,508±3,2407
Chromium (Cr)(μg/L)	0,031±0,031	0,902±0,902	0±0	0,013±0,0119
Iron (Fe)(μg/L)	106,725±26,143a	25,937±6,6756b	5,953±2,9547b	31,376±7,1885b
Manganese (Mn)(μg/L)	72,236±25,436b	82,544±13,920b	19,238±7,6393b	188,364±23,547a
Cobalt (Co)(μg/L)	0,016±0,016	0,093±0,093	0,014±0,0071	0,014±0,0093
Nickel (Ni)(μg/L)	0,118±0,0395b	0,215±0,2009ab	0±0b	0,675±0,1456a
Boron (B)(μg/L)	112,2±9,4695	165,802±48,723	79,927±12,179	122,662±7,4982
Tin (Sn)(μg/L)	5,598±0,3291a	5,403±1,4926a	1,96±0,3848b	2,266±0,6462ab
Aluminum (Al)(μg/L)	62,557±19,399a	6,412±0,9065b	3,584±0,7315b	6,81±1,2572b
Cadmium (Cd)(μg/L)	0±0	0±0	0±0	0,005±0,0034
Sulfur (S)(mg/L)	19,862±2,1221b	24,637±1,6075b	15,798±1,5578b	57,423±12,995a
Vanadium (V)(μg/L)	3,554±0,7822	2,185±0,4071	1,627±0,7683	2,241±0,5784
Titanium (Ti)(μg/L)	9,689±3,5487	3,46±3,46	0,097±0,0854	3,801±1,9483
Mercury (Hg)(μg/L)	0±0b	0,407±0,1155ab	0±0b	0,972±0,3247a
Arsenic (As)(μg/L)	3,086±0,4835ab	4,889±0,4789a	1,85±0,2648b	4,272±0,7596a
Selenium (Se)(μg/L)	0,431±0,0382c	0,268±0,0339d	1,268±0,0214a	0,683±0,0477b
Antimony (Sb)(μg/L)	0,927±0,0289b	1,16±0,0586a	0,01±0,0059d	0,41±0,0450c

The lowest Pb value was measured as 2,493 μg/L in Summer and the highest value as 15.517 μg/L in Winter. It is discussed that because of the areas where Kırklareli river intersects with the road, Pb mixed with rain water and the average lead Pb increases in winter months. Duman and others (2007) reported a study in the Lake Abant, the highest lead concentration was found at the 1st station, where the Mudurnu-Bolu highway intersects with the lake. As a result of the mixing of the exhaust gases from the cars with the rain water into the lake, it was thought that the Pb values were high in this station. Average annual Pb concentration measured as 36,92 μg/L. With the examinaton of seasonal averages of Pb concentrations, it was determined that the Pb accumulation in the spring season was higher than the other seasons. Turgut (2003) conducted that the Pb concentration in the water reached the highest value in November of the Küçük Menderes River. The lowest Fe value were measured as 5,953 μg/L in Summer, and the highest value was 106,725 μg/L in Winter. Due to the abundance of precipitation in the winter season, it is thought that the soil may be washed and the Fe content may be mobilized to water resources and rising the concentration. The lowest Mn concentrations were measured as 19,238 µg/L in the Summer season, and the highest value was 188,364 µg/L in the Autumn season. A study conducted in Abant Lake the annual average Mn concentration was found to be 34.86 µg/L. Duman and others (2007),he highest Mn concentration was determined as 119.43 µg/L in the autumn season. While the nickel value was below the detection limit in the summer season, the highest value was measured as 0.675 µg/L in the Autumn season. The highest nickel value was below the 1st Class quality value in terms of Quality Criteria According to the Classes of Inland Surface Water Resources. The lowest Sn value determined as 1,960 µg/L in Summer, and the highest as 5,598 µg/L in Winter. Kalıpcı and Ceylan (2017) reported in the study "Externals of heavy metal pollution in the Konya main discharge channel" total 7 season heavy metal results showed Sn parameters were the highest in the autumn period of 1.7 µg/L. The lowest Aluminum value was measured as 3,584 µg/L in Summer and the as 62,554 µg/L in Winter. Öztürk (2014) recorded the highest Al value as 18.00 µg/L at Apa Dam Lake Algaes in October 2011. According to study conducted by Kalıpcı and Ceylan (2017), heavy metal analysis results of a total of 7 points of the Konya main discharge channel, determined that the aluminum parameter was the highest 365 µg/L in the autumn period. The lowest total sulfur value was 15,798 mg/L in the Summer season, and the highest 57,423 mg/L in the Autumn season. It is thought that sulfur emissions increase with the autumn months as a result of the burning of fossil fuels used in residential heating in the city center. Increase of precipitation in these month sulphur causes the air pollution with the mix water resources. As a result increasing the amount of pollution. In addition, because of the closest position of water sources to the main road, exhaust emission gases have a positive effect on the sulfur value. The lowest value of arsenic was measured as 1.85 µg/L in the Summer season and the highest value was measured as 4.889 µg/L in the Spring season. Baig et al. (2009) stated that arsenic concentrations in all samples except the samples taken from Lake Manchar and its canal (Aral wah) which was exposed to human-induced pollution were below the 10 µg/L value recommended by WHO) in their study of surface waters in Jamshoro region, Pakistan. Baig et al. (2010) reported that arsenic concentrations in surface water in the Khairpur region ranged between 3.0-18.3 µg/L and the average concentration of arsenic was 8.0 µg/L in Pakistan. According to the our results related to arsenic concentrations do not exceed the values determined by WHO. In addition, these results were observed to be quite low on an annual average basis when compared to the literature. It was determined that there was no statistically significant difference between the seasonal averages of copper, zinc, chromium, cobalt, boron, cadmium, vanadium, titanium, mercury, selenium and antimony parameters ($p>0.05$). It was showed that the results of one-way analysis of variance on the basis of station for heavy metal parameters in water samples in Table 7. It was also investigated whether there was a statistically significant difference between stations for heavy metal parameters in water samples. In our analysis results, there was a statistically significant difference between the stations in terms of the measured values of the vanadium parameter ($p<0.05$). It is seen that the statistical difference between the groups originates from stations 9 and 10. The lowest value of vanadium was measured as 1.107 µg/L at Station 1, and the highest value was measured as 5.906 µg/L at Station 10. According to WHO, Vanadium in drinking water should not exceed 10µg/L (Poyraz, 2014). In present study, the amount of vanadium remained low considering the data of WHO. There was no statistically significant difference between stations in terms of measurement values of lead, copper, zinc, chromium, iron, manganese, cobalt, nickel, boron, tin, aluminum, cadmium, sulfur, titanium, mercury, arsenic, selenium and antimony elements ($p > 0.05$). It was present that the results of correlation analysis for heavy metal parameters in water samples in Table 8. In current study, it was determined that there was a statistically significant positive and quite strong relationship between lead and iron; between chromium and cobalt, nickel, boron, titanium; between aluminum and iron; between cobalt and nickel, boron, titanium; between nickel and boron, titanium. In addition, it was also detected that there was a statistically significant positive and strong relationship between lead and aluminum; between chrome and stannous (tin); between cobalt and stannous; between nickel and stannous, titanium; between boron and stannous, titanium.

Table 7. The results of one-way analysis of variance on the basis of station for heavy metal parameters in water samples (Gülocak, 2019)



Parameters	Stations									
	1	2	3	4	5	6	7	8	9	10
Lead (Pb)(µg/L)	10,05±2,485	1,561±0,523	4,417±0,842	4,258±0,987	6,335±2,909	8,317±4,490	8,222±4,371	10,48±2,790	3,803±1,493	3,298±1,992
Copper (Cu)(µg/L)	0,731±0,472	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Zinc (Zn)(µg/L)	8,865±4,824	4,265±2,968	1,882±1,882	1,948±1,948	1,648±1,016	1,265±1,265	0,211±0,211	4,881±4,443	0,401±0,401	0±0
Chromium (Cr)(µg/L)	3,925±3,854	0,001±0,001	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
Iron (Fe)(µg/L)	55,61±17,06	7,353±3,667	17,31±6,761	18,63±6,960	35,93±20,29	50,05±31,84	48,93±31,38	61,40±19,24	18,44±9,147	18,03±13,92
Manganese (Mn)(µg/L)	89,12±32,83	62,34±32,83	90,58±29,80	65,30±12,65	81,59±34,79	88,73±38,91	91,82±39,92	107,0±42,05	57,61±33,68	74,79±36,39
Cobalt (Co)(µg/L)	0,397±0,397	0±0	0±0	0±0	0,017±0,011	0,014±0,010	0±0	0±0	0,011±0,011	0,03±0,026
Nickel (Ni)(µg/L)	1,15±0,850	0,206±0,146	0,075±0,075	0±0	0,111±0,080	0,048±0,037	0,098±0,076	0,158±0,158	0,133±0,093	0,141±0,104
Boron (B)(µg/L)	324,8±211,3	160,7±11,78	115,4±11,14	115,0±10,98	108,8±10,79	86,94±12,49	85,47±11,94	87,56±13,50	93,25±13,34	107,5±6,514
Tin (Sn)(µg/L)	9,561±5,029	2,923±0,721	4,832±0,911	5,331±1,600	3,515±0,639	2,078±0,882	2,695±0,910	3,151±0,934	3,731±0,821	2,915±1,230
Aluminum (Al)(µg/L)	10,57±2,258	4,891±0,606	6,572±1,811	6,892±1,935	18,86±14,45	26,14±22,02	25,68±21,65	18,69±12,63	7,373±2,439	14,29±9,087
Cadmium (Cd)(µg/L)	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0,002±0,002	0±0	0,005±0,005
Sulfur (S)(mg/L)	28,80±4,245	31,23±5,708	21,55±3,890	19,43±2,828	20,31±3,851	19,28±4,007	19,53±4,078	21,26±4,456	43,98±18,97	46,27±17,93
Vanadium (V)(µg/L)	1,107±0,309b	1,246±0,498b	1,134±0,390b	1,271±0,406b	1,127±0,396b	1,827±0,476b	1,91±0,453b	1,748±0,445b	5,088±1,236a	5,906±1,251a
Titanium (Ti)(µg/L)	17,95±12,46	0,151±0,151	0,307±0,290	0,052±0,039	2,941±2,358	4,097±3,824	4,021±3,782	2,917±2,252	0,308±0,308	2,036±1,586
Mercury (Hg)(µg/L)	0,26±0,110	0,056±0,052	0,628±0,389	0,76±0,510	0,205±0,141	0,21±0,143	0,528±0,360	0,162±0,085	0,311±0,168	0,071±0,062
Arsenic (As)(µg/L)	3,897±1,963	2,998±0,697	3,041±0,601	3,594±0,691	3,545±0,730	2,934±0,582	3,035±0,613	2,971±0,584	5,873±0,952	6,323±1,358a
Selenium (Se)(µg/L)	0,731±0,167	0,513±0,197	0,535±0,190	0,532±0,189	0,638±0,169	0,604±0,166	0,681±0,182	0,665±0,179	0,611±0,144	0,531±0,152
Antimony (Sb)(µg/L)	0,822±0,644	0,786±0,502	0,588±0,403	0,808±0,600	0,635±0,440	0,65±0,466	0,674±0,436	0,674±0,477	0,768±0,500	0,833±0,562

* Differences between means with different lowercase letters on the same line are significant. ($p<0,05$)

Table 8. The results of correlation analysis for heavy metal parameters in water samples (Gülocak, 2019)

	Lead	Copper	Zinc	Chromium	İron	Manganese	Cobalt	Nickel	Boron	Tin	Aluminum	Cadmium	Sulfur	Vanadium	Titanium	Mercury	Arsenic	Selenium	Antimony
	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(mg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)	(µg /L)
Lead (µg/L)	.	0,042	0,212	,298*	,988**	0,109	,299*	,318**	,266*	,384**	,840**	0,027	-0,186	0,018	,638**	-0,056	-0,01	-0,15	0,166
Copper (µg/L)	.	.	0,125	-0,019	0,029	0,157	-0,025	0,136	-0,014	-0,069	-0,023	-0,03	0,102	-0,066	0,097	-0,007	-0,121	-0,013	-0,098
Zinc (µg/L)	.	.	.	,595**	0,195	0,208	,589**	,690**	,574**	,464**	-0,07	,259*	-0,072	-,274*	,539**	0,065	,378**	-0,098	,511**
Chromium (µg/L)	.	.	.	.	,276*	0,083	,997**	,927**	,982**	,842**	0,008	-0,022	-0,054	-0,121	,872**	0,072	,554**	0,018	,393**
Iron (µg/L)	.	.	.	.	.	0,089	,277*	,300*	,251*	,368**	,876**	0,029	-0,156	0,056	,630**	-0,061	0,029	-0,18	0,203
Manganese(µg/L)	.	.	.	.	.	.	0,098	,284*	0,136	0,058	-0,121	0,191	,244*	0,055	0,084	,282*	0,148	-0,229	-0,02
Cobalt (µg/L)	.	.	.	.	.	.	.	,925**	,977**	,836**	0,014	-0,025	-0,059	-0,103	,873**	0,068	,550**	0,027	,388**
Nickel (µg /L)	.	.	.	.	.	.	.	.	,922**	,735**	0,013	0,134	0,136	-0,091	,866**	0,137	,530**	0,046	,333**
Boron (µg/L)	.	.	.	.	.	.	.	.	.	,848**	-0,015	-0,018	0,018	-0,09	,842**	0,11	,581**	-0,061	,358**
Tin (µg/L)	.	.	.	.	.	.	.	.	.	.	0,14	-0,108	-0,097	-0,033	,780**	0,006	,530**	-0,2	,332**
Aluminum (µg /L)	.	.	.	.	.	.	.	.	.	.	.	-0,043	-0,13	0,202	,441**	-0,134	-0,077	-0,098	0,039
Cadmium (µg /L)	.	.	.	.	.	.	.	.	.	.	.	.	,542**	0,17	-0,015	-0,026	0,21	0,057	-0,036
Sulfur (mg/L)	.	.	.	.	.	.	.	.	.	.	.	.	.	,413**	-0,057	0,145	,381**	-0,035	-0,207
Vanadium (µg /L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	-0,041	-0,065	0,209	-0,152	-,341**
Titanium (µg /L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0,032	,431**	-0,002	,339**
Mercury (µg/L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0,134	-0,196	0,035
Arsenic (µg/L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	-,344**	,527**
Selenium (µg/L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	-,407**
Antimony (µg/L)	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.

*p<0,05, **p<0,01

CONCLUSION

In this study, it was investigated whether there is heavy metal pollution in Kırklareli Stream. Accordingly, it was determined to be of second-class quality in terms of lead and manganese, third class quality in terms of mercury, first class quality in terms of other heavy metals. It has been determined that mercury and its compounds in water are of great importance in terms of toxicity. These compounds can be diffuse because they are not soluble in water. Additionality, these compounds can dissolve in animal and vegetable fats and pass to aquatic primitive living creatures (Hammond, 1971). It has been seen that there is a rapid accumulation of mercury (Hg) in larger organisms living in polluted waters, since they are difficult to metabolize (Abelson, 1970, Beckert et al.,1974). There is mercury pollution that can be considered dangerous in the world. It has been observed that this pollution is especially great in closed seas and inland waters. All kinds of pollution in water can be added to the food chain (Şanlı, 1976). It is thought that the reason for the high amount of lead in the waters may have been mixed with the water from the road with precipitation although there is no serious industrial settlement around the creek. When the lead concentration in polluted waters is less than 100 µg/L, aquatic organisms are not affected much. It has been determined that 100-200 µg/L constitutes the toxicity limit for sensitive fish (this limit is 1000 µg/L in hardness water) (Mutluay, 1996, Cicik, 2003). When the lead values are less than 10 µg/L, it is first class quality according to CPCB. In present study, the highest lead value was found to be 15.52 µg/L in winter. For this reason, the lead is considered as second-class quality and it is thought that wastewater should be treated. It has been stated that manganese is the least toxic metal among the heavy metals. Manganese compounds are generally used in the production of iron and steel industry, while manganese dioxide and other manganese compounds are used in the manufacture of batteries, glass and fireworks (Durmaz, 2019). In addition, potassium permanganate, a manganese compound, passes into surface waters through the use of bleaching agent and cleaning (disinfection) (ATSDR 2000). It is stated as the limit value of 400 µg/L in terms of human health (WHO, 2011). Manganese ions are detected in wastewater and drinking water as dissolved. Manganese can be purified by conventional methods. In addition, manganese removal can be achieved by softening with lime, reverse osmosis, ion exchange and chemical precipitation methods (Bulus, 2021). In a study conducted by Bulus in 2021, it was stated that an industrial-sized nanofiltration to be produced for the removal of manganese in drinking water could be an important method. This method can also be provided for wastewater treatment plants with suitable conditions. When wastewater is purified and reused for irrigation in agriculture, accumulation of heavy metals with increasing concentrations in every organism becomes inevitable. In this context, this is a process that threatens all living organism. Therefore, appropriate collection of waste water and its safe use in agriculture after treatment should be encouraged. In this way, water is saved and water resources are not polluted, plant productivity increases, the need for artificial fertilizers decreases, waste water is removed in the most beneficial way without harming the nature.

ACKNOWLEDGEMENT

This study was produced from the first author's master's thesis.

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