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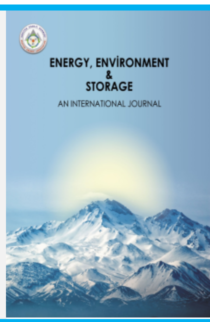

Seasonal Monitoring of Water Quality Parameters and Pesticides at the Altınapa Reservoir Watershed

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ABSTRACT. Altınapa Reservoir is a reservoir located on the Meram Stream in the Konya Province in Türkiye that supplies drinking water. The Altınapa Reservoir feeds the Konya Drinking Water Treatment Plant with 37.8 million m^3 of water annually and the treated water is delivered by the drinking water network. The aim of this study was to determine the effect of agricultural activities and settlements on water quality in the Altınapa Reservoir Watershed. In the study, major water quality parameters (pH, electrical conductivity, total organic carbon, total nitrogen, nitrite, nitrate, phosphorus, phosphate, and total suspended solids) and pesticides were monitored at four stations (K1, K2, K3, K4) on the sub-streams feeding reservoir. Major water quality parameters were monitored at monthly intervals for 12 months between June 2020 and May 2021, and pesticides were monitored seasonally at 4 seasons (Fall 2019, Winter 2020, Summer 2020, and Spring 2021). A correlation matrix was used to assess the connections between nine indicators of water quality. The annual average conductivity and pH values of the samples taken from four different stations of the Meram Stream were 432 µS/cm and 8.04, respectively. The highest value for total nitrogen was 10.73 mg/L and it was 0.87 mg/L for nitrate. Annual average total organic carbon values were determined as 1.35, 1.69, 1.51, and 1.46 mg/L at K1, K2, K3, and K4 stations, respectively. Specific UV absorbance indicated that organic matters of water are mostly hydrophilic and have low aromatic content. In seasonal pesticide monitoring, 71 different compounds were detected in water samples. The compounds whose concentrations exceeded Turkish Environmental Quality Standards were identified as DDD-op, DDE-p.p', diflufenican, and imidacloprid. Pesticides constitute most of the micropollutants detected in water samples. The highest positive correlation among water quality parameters was obtained between conductivity and nitrate (0.81) and total nitrogen (0.88).

Keywords: Altınapa Reservoir Watershed, Environmental quality standards, Drinking water, Micropollutants, Water Quality.

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1. INTRODUCTION

Water quality monitoring is essential for developing water management strategies, identification of pollution sources, and development of effective and economical treatment techniques [1-3]. The quality and quantity of water resources are very important for urban water supply, particularly in regions where water resources are limited [4]. Surface water resources, including lakes, reservoirs, and rivers, constitute a significant portion of drinking water resources. However, the deterioration of surface water quality due to the contamination as a result of human activities causes significant issues worldwide [5]. The World Health Organization (WHO) estimates that water contamination is responsible for 80% of human health problems [6].

Increase in the use of different types of chemicals and toxic substances in urban life, industry, and agriculture leads to the presence of micropollutants and industrial chemicals including pesticides, heavy metals, medicines, pharmaceuticals, personal care products, detergents, and disinfection by-products in water resources, even in treated water [7-9]. Due to bioaccumulation and transfer in the food chain, these micropollutants pose a concern to human health [10], have a negative impact on the aquatic biota, and reduce the efficiency and increase the cost of drinking water treatment [11]. By releasing the Water Framework Directive 2000/60/EC at the beginning of the 2000's, the European Union (EU) came up with a plan to identify priority compounds that pose a high hazard to the aquatic ecosystem. This plan aims to clean up micropollutants in water resources. The European Union's 2008/105/EC water policy directive resulted in the development of a list of 33 priority compounds and substance categories. The efforts led to an update of the water framework policy by the European Parliament and, as a result, identification of a 45-item list of priority items/groups of items [12, 13].

Three substances are recommended for the first watch list of sub-components in the directive 2013/39/EC, along with a number of pesticides (aldrin, dichlorodiphenyl trichloroethane, dicofol, dieldrin, endrin, endosulfan, isodrine, heptachlor, lindane, pentafluorophenol, chlorpyrifos, chlorfenvinphos, dichlorvos, atrazine, simazine, terbutrine, diuron, isoproturon, trifluralin, alacyper), solvents (dichloromethane, dichloroethane, trichloromethane and carbon tetrachloride), perfluorooctane sulfonic acid and its derivatives, polychlorinated biphenyls, polycyclic aromatic hydrocarbons. In addition to nonylphenol and octylphenol, three compounds (diclofenac, 17-alpha-ethinylestradiol (EE2) and 17-beta-estradiol (E2)) were included in the recommendation for the first watch list for sub-components. Additionally, this directive defines several specific pesticides, including acloniphene, bifenox, sibutrin, quinoxifen, organotin compounds (tributyltin), dioxins and dioxin-like compounds, brominated diphenylethers, hexabromocyclododecanes, and di(2-ethylhexyl) phthalate. The directive of 2013/39/EC specify that it is critical to monitor novel pollutants that are not often addressed in monitoring programs but may have ecotoxicological and toxicological consequences, even if the majority of micropollutants has no discharge limits.

In the Surface Water Quality Management Regulation (Türkiye), 250 micropollutants are listed and the Environmental Quality Standards are defined for these micropollutants in rivers, lakes, coastal and transitional waters [14]. Within the scope of the Regulation on the Quality and Treatment of Drinking Water Supply in Türkiye, 99 water quality parameters are monitored at the inlets and outlets of drinking water sources, and water resources are classified according to A1, A2 and A3 categories with distinct guideline values [15]. In addition to the criteria for water quality outlined in this rule, guiding values are also provided for several micropollutants. Selek [16] collected samples from 287 surface water basins nationwide in Türkiye four times a year to conduct a comprehensive site-specific monitoring analysis. In this study, the evaluation of water quality revealed that one water source in the Eastern Black Sea Basin was in A1 water quality, 93 water sources were in A2 water quality, and 193 water sources were in A3 water quality categories. They concluded that despite a pressure regarding micro-contaminants in Türkiye's surface water resources, the issue is more dominating in terms of microbiological quality as well heavy metals from geological formations in certain sites [16]. Canli et al. [17] evaluated water quality in terms of micropollutants in 600 samples collected from Alibeykoy Reservoir (Istanbul), Omerli Reservoir (Istanbul), Sapanca Lake (Sakarya), and the effluent of wastewater treatment plant (Istanbul). It was determined that five most often detected substances in the samples were acetochlor, acetamiprid, thiamethoxam, carbendazim, and terbutryn [17]. Emadian et al. [18] examined 300 samples for 222 organic micropollutants taken from 75 different stations along the Ergene River between August 2017 and May 2018. A total of 165 micropollutants with concentrations ranging from 1.90 ng/L to 1824.55 µg/L were detected.

Yavuz et al. [19] grabbed samples from three major components of the drinking water system, including the raw water sources (the Camlidere and Kesikkopru Reservoirs), the drinking water treatment plant (the Ivedik Water Treatment Plant), and the water distribution network, to evaluate the seasonal fluctuations in biocide levels and their association with general water quality indicators. Triclosan concentrations found in surface water samples were 0.65–11.15 ng/L and 0.8–48.96 ng/L, respectively, for the Camlidere and Kesikköprü Reservoirs. The range of chlorhexidine concentrations was 1.33 to 5.31 ng/L. The results of the treatment plant effluent analysis revealed that the level of all biocides in the distribution network was below the quantification limit. During a hydrological year (February 2017–January 2018), Ustaoglu et al. [20] conducted research at three chosen monitoring stations in the Turnasuyu Basin to determine the impacts of residential pollution and agricultural activities on water quality. The findings demonstrated that Turnasuyu Stream has extremely high-water quality and the trace elements found are not riskily close to the public health threshold.

In recent years, the importance of monitoring and assessing the water quality has increased due to worries based on indicators showing that fresh water has become increasingly scarce. Monitoring of water quality is an effective method to determine the effects of pollution sources, as well as to ensure the effective use and management of water resources and the maintenance, and also protection of aquatic life [21].

Altınapa Reservoir, located on the Meram Stream in Konya, Türkiye, was built between 1963-1967 by The State Hydraulic Works to provide drinking and utility water, delivers irrigation service to an area of 1,400 hectares and supplies about 38 million m^3 water which is about one-third of Konya's total drinking water demand. Meram Stream, with an annual average flow of approximately 1 m^3/s, is the mainstream feeding the reservoir. The reservoir has an average capacity of 15,000 million m^3 and a surface area of 2.3 km^2. Since the reservoir is a resource for drinking water and other supplies, the reservoir and its basin have been taken under protection and measures against contamination have been adopted.

The aim of this study is to monitor water quality based on major water quality parameters and pesticides and to evaluate water quality at the Altınapa Reservoir Watershed. Besides, the relationships between nine water quality parameters were evaluated by a correlation matrix. In the scope of monitoring at four stations on the sub-streams feeding Altınapa Reservoir pH, electrical conductivity (EC), total organic carbon (TOC), UV absorbance at 254 nm (UV_{254}) wavelength, total nitrogen (TN), nitrite (NO_2^-), nitrate (NO_3^-), total phosphorus (TP), phosphate, total suspended solids (TSS), and pesticides were monitored. Major water quality parameters were monitored monthly for 12 months between June 2020 and May 2021, and pesticides were monitored seasonally for 4 seasons (in months September 2019, January 2020, August 2020, and April 2021). Pesticide contamination was evaluated based on Turkish Environmental Quality Standards (EQS). The associations between water quality parameters were examined by a correlation matrix.

2. MATERIALS AND METHODS

2.1 Sample Collecting and Analytical Methods

2 L water samples were collected at the Altınapa Reservoir Watershed at four monitoring stations (K1, K2, K3, K4) between June 2020 and May 2021 (Figure 1). The water samples were transported within 24 hr to the laboratory in a cooler containing ice cubes, kept at +4ºC in a fridge for experimental studies. Table 1 presents the specifics of analysis techniques for water quality parameters. The physicochemical analyses of water samples were conducted according to the Standard Methods [22]. TOC and total nitrogen were determined according to SM 5310 B [36] using a TOC analyzer (TOC-L CPH, Shimadzu). The UV absorbance of water samples at a wavelength of 254 nm were measured using UV-visible spectrophotometer (Hach Lange DR 6000) according to the SM 5910 B method [22]. Nitrite, nitrate, TP, and phosphate were analyzed by Suleyman Demirel University Geothermal Energy Groundwater and Mineral Resources Research and Application Center. Figure 1 shows the watershed boundary and water quality monitoring stations at the Altınapa Reservoir Watershed. Pesticides were analyzed by the Scientific and Technological Research Council of Türkiye (TUBITAK), Marmara Research Center Laboratory. LC-MSMS and GC-MSMS equipment were used for the pesticides analyses, and the limit of quantification values were given as 0.001 g/L.

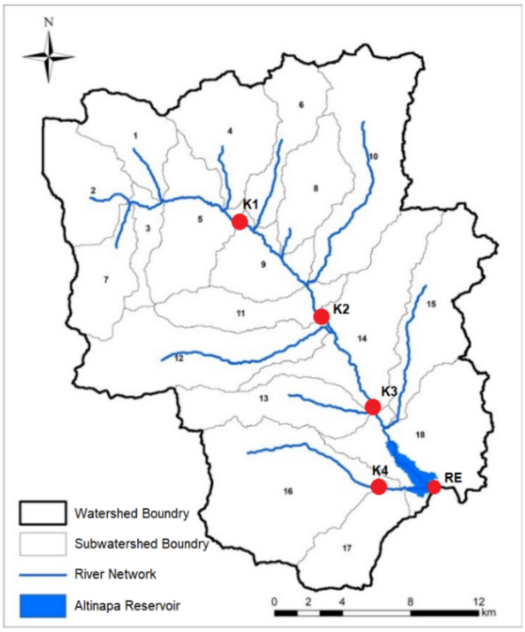

Figure 1. Watershed boundary and water quality monitoring stations at the Altınapa Reservoir Watershed.

Specific UV absorbance (SUVA), which is a normalized parameter, is used to compare various natural organic matter (NOM) properties of different water sources. SUVA values of samples were computed by dividing UV absorbance at a certain wavelength to TOC content. Equation 1 explains the SUVA computation.

$$SUVA_{254} = UV_{254}/TOC * 100 \quad (1)$$

In equation 1, $SUVA_{254}$ (L/mgTOC.m) represents the specific UV absorbance, UV_{254} (cm^{-1}) represents the absorbance at 254 nm wavelength and TOC (mg/L) represents the total organic carbon concentration.

Table 1. Analytical methods and detection limits of water quality parameters

Parameter	Unit	Methods	Equipment	MDL
pH		SM 4500 H+	WTW Multi340i/Set	
EC	µS/cm	SM2510B	WTW Multi340i/Set	
TOC	mg/L	SM5310B	TOC-L CPH Shimadzu	0.1
TN	mg/L	High temperature burning	TOC-L CPH Shimadzu	
UV_{254}	cm^{-1}	SM5910	UV-1700 Shimadzu	±0.005
NO_3-N NO_2-N	mg/L	USEPA Metot 300	Dionex ICS-3000	0.01
$SUVA_{254}$	L/mg TOC.m	UV_{254}/TOC		

4. RESULTS AND DISCUSSIONS

4.1. Water Quality Results

The pH levels of samples ranged from 7.68 to 8.39. Figure 2 displayed seasonal variations of pH values at the monitoring stations and the findings demonstrated that the pH value variations were rather small. During the sampling period, the highest pH value was measured at the K4 monitoring station as 8.39 in September, and the lowest pH value was measured at K1 monitoring stations as 7.68 in January. The pH range of the waters meets the standards in the "Regulation on Water Intended for Human Consumption" established by the Türkiye Republic Ministry of Health [23]. Similar pH ranges were discovered in earlier investigations in Apa Reservoir in Konya [24-26].

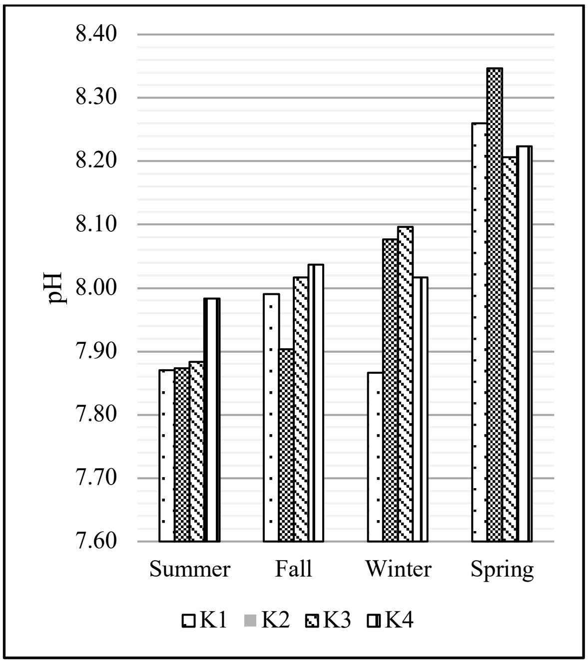

Figure 2. Seasonal average pH values variations at monitoring stations.

Conductivity is a numerical expression of the electric current carrying capacity of an aqueous solution. Conductivity is an indicator parameter that is also used for monitoring pollution in general. The conductivity value of natural rivers and lakes varies between 10-1000 µS/cm. Values above this level indicate that these surface waters are polluted. The conductivity measurement values at the monitoring stations vary between 315 µS/cm and 644 µS/cm (Table 2). The highest conductivity values at the monitoring stations were measured at 644 µS/cm K2 station in August, and the lowest at 315 µS/cm K4 station in August, respectively.

NOM is a heterogeneous mixture containing macro-molecular humic structures, small molecular weight hydrophilic acids, proteins, fats, carboxylic acids, amino acids, carbohydrates, and organic substances such as hydrocarbons, and TOC is an indicator of NOMs [27]. Annual average TOC values were determined as 1.35, 1.69, 1.51 and 1.46 mg/L at K1, K2, K3 and K4 stations, respectively. An increase in the TOC concentration of all monitoring stations was observed in January and February. The increase in TOC values might be attributed to the transport of organic materials to the reservoir by surface runoff due to seasonal precipitation. The natural components of organics are humic acid, fulvic acid, amines, and urea, while synthetic sources include certain detergents, industrial chemicals, pesticides, fertilizers, herbicides, and chlorinated organics [28]. High concentrations of organic matter (TOC>2-3 mg/L) are not desired, especially in drinking water sources. High TOC concentrations in drinking water increase the dose of coagulant, lead to the formation of disinfection by-products, cause microbial growth in the network, as well as cause competition in the removal of micropollutants such as pesticides in treatment processes [29]. Therefore, it is important to monitor TOC values in drinking water sources and to treat them especially before the disinfection process in order to manage water treatment and its distribution in the network in a safe and economical way [30].

Non-specific parameters such as UV absorbance at wavelengths of 254-280 nm are used to characterize NOMs [27, 31]. A strong correlation was found between the aromatic carbon content of the water sample and the UV absorbance. By measuring the UV absorbance of NOM solutions in the range of 254-280 nm, the amount of aromatic compounds (unsaturated double bonds and π-π electron interactions) in water is indirectly determined by the general absorbance value [31, 32]. The highest and lowest UV_{254} absorbance were detected at K3 and K1 stations, and UV_{254} absorbance values were measured as 0.050 cm^{-1} and 0.019 cm^{-1}, respectively. Annual average UV_{254} absorbance values at stations K1, K2, K3 and K4 feeding the reservoir were 0.028, 0.035, 0.035 and 0.030 cm^{-1}, respectively.

As the NOM is a heterogeneous mixture of different organic compounds, the measured SUVA is an average value showing the distribution of chromophores (double bonds and/or aromatic structures) in the NOM. As well, the obtained ratios describe the hydrophilic and hydrophobic properties of NOM in water [31, 33]. In a water sample, $SUVA_{254}$>3.5-4 L/mg-m indicates mainly hydrophobic and especially aromatic material, while water with $SUVA_{254}$<3 L/mg-m indicates mainly hydrophilic material [33, 34]. Figure 3 presented the seasonal variations of the SUVA values of monitoring stations. The $SUVA_{254}$ values calculated in the samples varied on a monthly basis. The highest $SUVA_{254}$ value was observed at 3.80 L/mg-m at the K3 station in November, and the lowest at 1.02 L/mg-m at the K2 station in February. In general, $SUVA_{254}$ is <3 L/mg-m at monitoring stations and is hydrophilic. Although the TOC values are higher in the winter months than the TOC values in the autumn months, the low SUVA values in the winter indicate that organic fractions with low aromatic content are transported to the surface waters with precipitation. On the other hand, low TOC and high SUVA values in autumn indicate that low molecular weight relatively hydrophilic organics degrade with temperature in summer.

Table 2. Water quality parameters at monitoring stations on the Meram Stream

Parameters		Monitoring Station			
		K1	K2	K3	K4
Conductivity (µS/cm)	Annual Average	457	476	449	344
	Minimum	326	325	328	315
	Maximum	544	644	570	380
TSS (mg/L)	Annual Average	5.36	4.00	9.27	2.25
	Minimum	1.00	0.00	0.00	1.00
	Maximum	28.0	23.0	49.0	3.0
UV_{254} (cm^{-1})	Annual Average	0.03	0.04	0.04	0.03
	Minimum	0.02	0.02	0.02	0.02
	Maximum	0.04	0.05	0.05	0.04
TOC (mg/L)	Annual Average	1.35	1.69	1.51	1.46
	Minimum	0.75	1.02	1.09	0.83
	Maximum	2.57	2.55	2.43	2.70
NO_2-N (mg/L)	Annual Average	0.30	0.18	0.12	ND
	Minimum	0.04	0.06	0.09	ND
	Maximum	0.58	0.57	0.14	ND
TP (mg/L)	Annual Average	0.06	0.09	0.06	0.06
	Minimum	0.06	0.09	0.05	0.06
	Maximum	0.06	0.09	0.06	0.06
PO_4 (mg/L)	Annual Average	ND	ND	ND	ND
	Minimum	ND	ND	ND	ND
	Maximum	ND	ND	ND	ND

TN is the sum of total Kjehdahl nitrogen (organic nitrogen and ammonia-N), ammonium-N, nitrate-N, and nitrite-N. The main pollutant sources of TN in water resources are domestic wastewater discharge, fertilizers applied in agricultural activities, and industrial wastewater discharges. Annual average values of TN concentration at monitoring stations of Meram Stream varied in the range of 0.01-4.87 mg/L. The highest TN concentration was measured at the K2 station in August with 10.73 mg/L, and the lowest at K4 station in September with 0.24 mg/L, respectively. Annual mean TN values at the stations K1, K2, K3 and K4 feeding the reservoir were determined as 1.98, 4.81, 3.32, and 0.63 mg/L, respectively. According to the results, there is no serious pollution in the Altınapa Reservoir Watershed in terms of TN. The reason might be attributed to that Altınapa Reservoir Watershed is a relatively closed and small basin, only agricultural activities are carried out in the basin. There are 5-6 small settlements and there is no serious wastewater flow from these areas and there is no industrial activity.

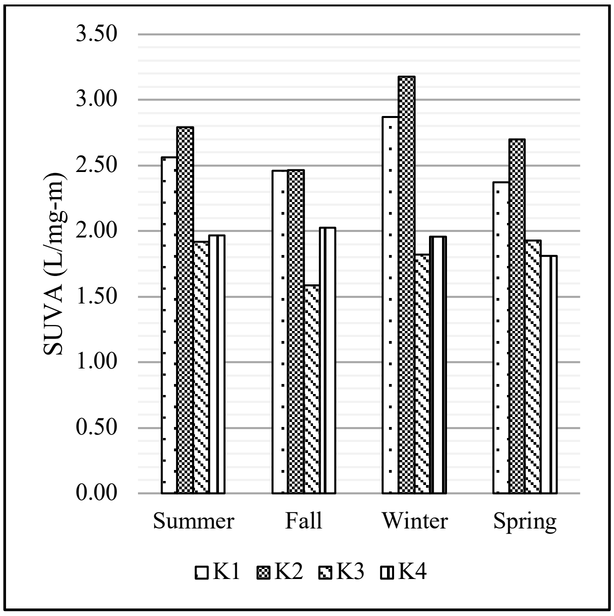

Figure 3. Seasonal average SUVA variations at the monitoring stations.

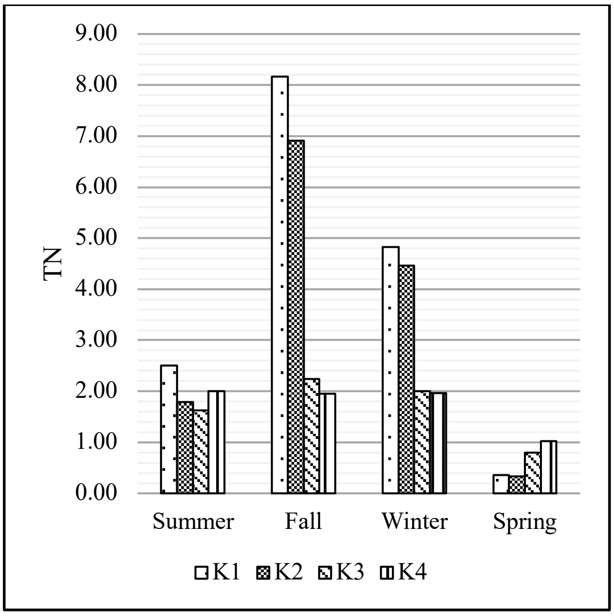

Figure 4. Seasonal average TN variations at the monitoring stations.

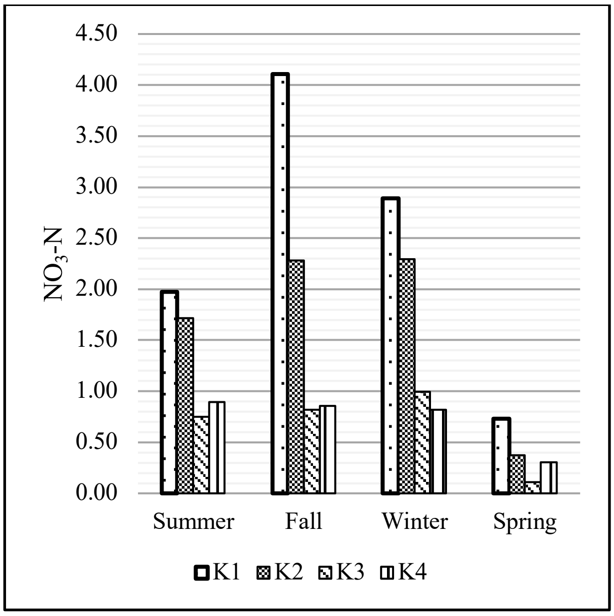

Figure 5. Seasonal average nitrate variations at the monitoring stations.

The annual average nitrate concentration was determined as 1.33, 2.02, 1.82 and 0.43 mg/L in K1, K2, K3 and K4, respectively (Figure 5). The highest nitrate concentration was observed at the K2 station with 4.87 mg/L in August and at the K3 station with 4.75 mg/L in September, while the lowest was detected at the K4 station with 0.01 mg/L in April. The nitrate concentration increase at some stations is thought to be due to agricultural activities or wastewater discharges close to the sampling stations. On the other hand, the highest nitrite concentration was measured at the K1 station in April with 0.58 mg/L. The maximum nitrite content was recorded at the K1 station in April during the monitoring period with 0.58 mg/L. However, it was found to be below the detection limit (<DL) of 0.01 mg/L at all stations in the annual monitoring in June, July, December, January, February, March and May.

The highest TSS value at the monitoring stations was 49 mg/L, and the lowest was 1 mg/L in April at the K4 station. However, TSS could not be found between August 2020 and February 2021 at the K4 station. The TSS values of K1, K2, and K3 stations also showed an increase in April. The severe rains and increased surface runoff are believed to be the reasons for this increase.

Fertilizers, animal and human waste, and garden waste all contain TP. There is no atmospheric (gaseous) form of TP. Due to the lack of atmospheric phosphorus cycling and the scarcity of phosphorus natural sources, phosphorus is frequently a limiting component in water systems [35]. Algae blooms in lakes and reservoirs are caused by TP, which comprises both dissolved and particulate forms of phosphorus. Except for August, the highest TP concentration of 0.09 mg/L was recorded at K2. However, since TP remained below the detection limit at all stations except August and September, the values in Table 2 include August and September.

Pesticides were monitored for 4 seasons in the months September 2019, January 2020, August 2020, and April 2021. The results of pesticides analyses were presented in Table 3. 71 different micropollutants including pesticides were detected. Pesticides detected in the reservoir effluent and/or at least at two monitoring stations were selected and presented in Table 3. The data belonging to the spring period is not shown in table, because any of compounds except acetamiprid could not be detected at least at two stations. Acetamiprid, aldrin, BHC-alpha, bromopropylate, ethoprophos, permethrin, piperonyl butoxide, and terbutryn were found in almost every station as well as reservoir effluents. In addition, acetamiprid, permethrin, piperonyl butoxide, and terbutryn were detected at least in two seasons. Moreover, the levels of DDD-op, DDE-p.p', diflufenican, and imidacloprid were higher than Türkiye's EQS.

Because they are carcinogenic, mutagenic, and teratogenic, pesticides have negative effects on both human health and aquatic life. Furthermore, because of their capacity to bioaccumulate in organism tissues and spread to higher species, they are extremely poisonous. To avoid pesticide infiltration and pesticide pollution in water resources, it is necessary to regulate agricultural activities and pesticide applications. Controlling pesticides at the source, handling them safely, managing waste pesticides and empty containers, setting up catchments to delay and slow runoff, building vegetated waterways and buffer strips, planning irrigation, and applying pesticides on schedule are the fundamental precautions that can be used to prevent pesticide pollution.

Table 3. Pesticides identified at the Altınapa Reservoir Watershed and their concentrations at monitoring stations

Pesticides	Type of Pesticides	EQS[a] (µg/L)	Autumn 2019 (µg/L)					Winter 2020 (µg/L)					Summer 2020 (µg/L)				
			K1	K2	K3	K4	RE[b]	K1	K2	K3	K4	RE[b]	K1	K2	K3	K4	RE[b]
Acetamiprid	Insecticide	42	0.0020	0.0058									0.0007		0.0011		0.0005
Aldrin	Insecticide	0.01											0.0007	0.0007	0.0054		0.0011
Azoxystrobin	Fungicide	0.20	0.0005	0.0007													
BHC-alpha	Insecticide	-											0.0023	0.0014	0.0015	0.0003	0.0003
Bromopropylate	Acaricide	0.12										0.074	0.0075	0.0006	0.0208	0.0000	0.0036
DDD-op	Insecticide	0.025						0.017	**0.065**		**0.058**	**0.061**					
DDE-p.p'	Insecticide	0.02											0.0098	0.0025	**0.0372**	0.0022	
Diflufenican	Herbicide	0.010							**0.044**			**0.070**					
Ethoprophos	Nematicide, insecticide	0.21	0.0311	0.0278		0.1410	0.0198										
Imidacloprid	Insecticide	0.14	0.0543	**0.3577**													
Metalaxyl	Fungicide	17	0.0169	0.0123													
Metrafenone	Fungicide	12							0.937			0.038					
Permethrin	Insecticide	0.12						0.011	0.036	0.012	0.039	0.084	0.0010		0.0179		0.0021
Piperonyl butoxide	Pesticide synergist	3.3						0.011	0.041		0.046	0.059	0.0254		0.1337		
Prometryne	Herbicide	0.3	0.0022	0.0027													
Tebuconazole	Fungicide	23	0.0289	0.0463													
Terbuthylazine	Herbicide	0.2	0.0061	0.0054													
Terbutryn	Herbicide	0.065	0.0091	0.0183	0.0073	0.0045	0.0071						0.0036	0.0024	0.0282	0.0026	0.0020
Tolclofos Methyl	Fungicide	1.2											0.0005		0.0024		

[a]EQS: Environmental Quality Standards [42]

[b]RE: Reservoir Effluent

4.2. Compositional Relations of Water Quality Parameters

A correlation matrix of nine parameters, namely, pH, conductivity, TSS, UV absorbance, TOC, TN, SUVA, nitrite, nitrate, was constructed and was shown in Table 4. Nitrate exhibited a significant positive correlation with TN (0.91) and conductivity (0.88). Similarly, a significant positive linear correlation with TN and conductivity (0.81) was detected. There is often a relationship between the conductivity of water and the total nitrogen and nitrate concentrations in the water. Conductivity is a measure of the water's ability to conduct an electrical current, which is influenced by the presence of dissolved ions in the water samples [36]. Nitrate is a common ion found in water that can contribute to the conductivity of the water [37]. Therefore, as the concentration of nitrate increases, the conductivity of the water tends to increase. Similarly, TN includes various forms of nitrogen, including nitrate [37]. As the concentration of TN increases, the concentration of nitrate in the water may also increase, leading to a corresponding increase in conductivity [38].

It is worth noting that the relationship between conductivity and nitrogen/nitrate concentrations can vary depending on other factors that may be present in the water, such as dissolved organic matter and other ions. Therefore, while conductivity can be a useful indicator of nitrogen/nitrate levels in water, it is important to also measure these nutrients directly to fully understand water quality. The UV_{254}. parameter showed moderate positive correlation with TOC (0.40), TN (0.52), and nitrate (0.34). TSS had moderate positive correlation with UV_{254}. (0.39) and TOC (0.31) and this can be explained by suspended solids in water that can come from a variety of sources, including natural and anthropogenic (human-made) sources [39].

Table 4. Correlation matrix of nine parameters of water quality

	pH	EC	SS	UV_{254}	TOC	TN	SUVA	Nitrite	Nitrate
pH	1								
EC	-0.67	1							
TSS	-0.23	-0.20	1						
U	-0.03	0.16	0.39	1					
TOC	0.12	-0.49	0.31	0.40	1				
TN	-0.51	0.81	0.01	0.52	-0.04	1			
SUVA	-0.15	0.61	-0.02	0.32	-0.73	0.38	1		
Nitrite	0.58	-0.75	0.23	0.21	0.59	-0.57	-0.66	1	
Nitrate	-0.56	0.88	0.03	0.34	-0.36	0.91	0.59	-0.62	1

Some natural sources of suspended solids include erosion of soil and rock, organic matter from decaying plants and animals, and algae blooms [40]. Anthropogenic sources of suspended solids include urban and agricultural runoff, wastewater discharge, construction activities, and mining activities [41]. Suspended solids can have harmful effects on aquatic ecosystems and human health if they are present in high concentrations [42]. Therefore, it is important to properly manage and reduce the sources of suspended solids in water sources. This can include implementing erosion control measures, reducing fertilizer and pesticide use, properly disposing of wastewater, and minimizing soil disturbance during construction activities.

5. CONCLUSIONS

In the Altınapa Reservoir Watershed, a total of 6018 people live in six little settlements. Agricultural activities and animal husbandry practices as well as wastewater discharges have impacts on the water quality of Altınapa Reservoir and the streams in the basin. In this study, the water quality of Meram Stream, which feeds the Altınapa Reservoir, was monitored in terms of major water quality parameters and pesticides for 1 year in the 2020-2021 period.

All water samples had pH values between 7.8 and 8.4 and conductivity values between 315 and 644 µS/cm. The TOC, nitrogen, and phosphorus species were used to evaluate the organic load in the basin. The continuous inflow of organic matter into the reservoir and the degradation of waste organics accumulated in the sediment over time resulted in a higher organic load at reservoir effluent than Meram Stream. The values of UV_{254} and SUVA of the water samples indicated that the organic compounds in the water source are hydrophilic and aliphatic. In contrast to the TOC values, the TN concentration was found to be lower at the reservoir effluent than at the waters from monitoring stations on Meram Stream. While nitrite was not found in all water samples, nitrate levels ranged from 0.01 to 4.87 mg/L throughout the year. Except for August and September 2020, total phosphorus and phosphate were not detected in the water samples. TSS levels in all samples were observed to be in the range of 2-98 mg/L.

The pesticide screenings revealed a total of 71 pesticides at various stations and seasons, although their concentrations were not higher than the EQSs. 8 of these pesticides were insecticides, 5 of them were fungicides, 4 of them were herbicides, 1 of them was an acaricide and 1 of them was a pesticide synergist.

Significant positive linear associations between conductivity and nitrate and TN were observed. Similar to that, there was a strong positive linear association between nitrate and TN.

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REFERENCES

[1] E.T. Aisien, E. Gbegbaje-Das II and F.A. Aisien. Water quality assessment of river Ethiope in the Niger-delta coast of Nigeria. Electronic Journal of Environmental, Agricultural & Food Chemistry. 9 (11), 1739-1745, 2010.

[2] O.A.A. Eletta. Water quality monitoring and assessment in a developing country. Water Quality Monitoring and Assessment, IntechOpen.**:** 481-494, 2012.

[3] J.O. Ighalo and A.G. Adeniyi. A comprehensive review of water quality monitoring and assessment in Nigeria. Chemosphere. 260, 2020.

[4] C.J. Vorosmarty, P.B. McIntyre, M.O. Gessner, D. Dudgeon, A. Prusevich, P. Green, S. Glidden, S.E. Bunn, C.A. Sullivan, C.R. Liermann and P.M. Davies. Global threats to human water security and river biodiversity Nature. 468 (7321), 334-334, 2010.

[5] R. Reservoiro and P. Icka. Evaluation of Water Quality Index for Drinking Water. Pol J Environ Stud. 22 (4), 1045-1051, 2013.

[6] Y.M. Zhang, J. Chen, L.Q. Wang, Y.L. Zhao, P. Ou and W.L. Shi. Establishing a method to assess comprehensive effect of gradient variation human health risk to metal speciation in groundwater. Environ Pollut. 241, 887-899, 2018.

[7] S.T. Glassmeyer, E.T. Furlong, D.W. Kolpin, A.L. Batt, R. Benson, J.S. Boone, O. Conerly, M.J. Donohue, D.N. King, M.S. Kostich, H.E. Mash, S.L. Pfaller, K.M. Schenck, J.E. Simmons, E.A. Varughese, S.J. Vesper, E.N. Villegas and V.S. Wilson. Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States. Sci Total Environ. 581, 909-922, 2017.

[8] R. Troger, P. Klockner, L. Ahrens and K. Wiberg. Micropollutants in drinking water from source to tap - Method development and application of a multiresidue screening method. Sci Total Environ. 627, 1404-1432, 2018.

[9] P.A. Neale, C. Feliers, L. Glauch, M. König, C. Lecarpentier, R. Schlichting, S. Thibert and B.I. Escher. Application of in vitro bioassays for water quality monitoring in three drinking water treatment plants using different treatment processes including biological treatment, nanofiltration and ozonation coupled with disinfection. Environmental Science: Water Research & Technology. 6 (9), 2444-2453, 2020.

[10] R. Miniero, V. Abate, G. Brambilla, E. Davoli, E. De Felip, S.P. De Filippis, E. Dellatte, S. De Luca, R. Fanelli, E. Fattore, F. Ferri, I. Fochi, A.R. Fulgenzi, N. Iacovella, A.L. Iamiceli, D. Lucchetti, P. Melotti, I. Moret, R. Piazza, A. Roncarati, A. Ubaldi, S. Zambon and A. Di Domenico. Persistent toxic substances in Mediterranean aquatic species. Sci Total Environ. 494, 18-27, 2014.

[11] C. Teodosiu, A.F. Gilca, G. Barjoveanu and S. Fiore. Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment. J Clean Prod. 197, 1210-1221, 2018.

[12] EU (2013). Directive 2013/39/EC of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy Text with EEA Relevance Off J L. E. Union, European Union. 226, pp. 1-17.

[13] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira and A.M.T. Silva. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environ Int. 75, 33-51, 2015.

[14] MoFWW (2015). Ministry of Forest and Water Works (MoFWW). Surface Water Quality Management. Ankara, Turkey, Official Gazette. 29327.

[15] MoAF (2019). Ministry Of Agriculture and Forestry (MoAF). Regulation on the Quality and Treatment of Drinking Water Supply. Ankara, Turkey, Official Gazette. 30823.

[16] B. Selek. Assessment of Surface Drinking Water Resources of Turkey in Terms of Water Quality Standards. J Water Chem Techno+. 42 (5), 415-426, 2020.

[17] O. Canli, E.O. Olgun, B. Guzel and M. Kaplan. Sensitive and accurate determination of 168 micropollutants including pharmaceuticals and pesticides in surface water and wastewater samples with direct injection using jet stream ESI LC-MS/MS. Int J Environ an Ch, 2022.

[18] S.M. Emadian, F.O. Sefiloglu, I.A. Balcioglu and U. Tezel. Identification of core micropollutants of Ergene River and their categorization based on spatiotemporal distribution. Sci Total Environ. 758, 2021.

[19] M. Yavuz, M. Oggioni, U. Yetis and F.B. Dilek. Biocides in drinking water system of Ankara, Turkey. Desalin Water Treat. 53 (12), 3253-3262, 2015.

[20] F. Ustaoglu, Y. Tepe and B. Tas. Assessment of stream quality and health risk in a subtropical Turkey river system: A combined approach using statistical analysis and water quality index. Ecol Indic. 113, 2020.

[21] R.O. Strobl and P.D. Robillard. Network design for water quality monitoring of surface freshwaters: A review. J Environ Manage. 87 (4), 639-648, 2008.

[22] APHA/AWWA/WEF (2012). Standard Methods for the Examination of Water and Wastewater, 20th Edition. APHA, AWWA and WEF. Washington, DC, American Public Health Association.

[23] THOM. Turkish Ministry of Health (TMOH), Regulation Concerning Water Intended for Human Consumption, Official Gazette, No. 25730, Ankara, Turkey (2005).

[24] R. Mert, S. Bulut and K. Solak. Investigation of some physical and chemical properties of Apa Reservoir Lake (Konya). Afyon Kocatepe University Journal of Science and Engineering. 2, 1-10, 2008.

[25] B.Y. Öztürk and C. Akköz. Investigation of water quality of Apa Reservoir Lake (Çumra-Konya) and according to the evaluation of PCA. Biodicon. 7 (2), 136-147, 2014.
[26] M. Diri. Monitoring Alteration of The Konya Closed Basin's Surface Water Quality. MSc Thesis (In Turkish), Necmettin Erbakan University, 2018.
[27] M. Kitis, T. Karanfil, J.E. Kilduff and A. Wigton. The reactivity of natural organic matter to disinfection byproducts formation and its relation to specific ultraviolet absorbance. Water Sci Technol. 43 (2), 9-16, 2001.
[28] R.A. Al Dwairi, K.M. Ibrahim and H.N. Khoury. Potential use of faujasite-phillipsite and phillipsite-chabazite tuff in purification of treated effluent from domestic wastewater treatment plants. Environ Earth Sci. 71 (12), 5071-5078, 2014.
[29] A. Matilainen, M. Vepsalainen and M. Sillanpaa. Natural organic matter removal by coagulation during drinking water treatment: A review. Adv Colloid Interfac. 159 (2), 189-197, 2010.
[30] Y. Hashempour, M. Nasseri, A. Mohseni-Bandpei, S. Motesaddi and M. Eslamizadeh. Assessing vulnerability to climate change for total organic carbon in a system of drinking water supply. Sustain Cities Soc. 53, 101904, 2020.
[31] N. Ates, M. Kitis and U. Yetis. Formation of chlorination by-products in low-SUVA surface waters: Correlations with SUVA and differential UV spectroscopy. Abstr Pap Am Chem S. 233, 416-416, 2007.
[32] S. Faixo, N. Gehin, S. Balayssac, V. Gilard, S. Mazeghrane, M. Haddad, G. Gaval, E. Paul and J.C. Garrigues. Current trends and advances in analytical techniques for the characterization and quantification of biologically recalcitrant organic species in sludge and wastewater: A review. Anal Chim Acta. 1152, 2021.
[33] J.K. Edzwald and J.E. Tobiason. Enhanced coagulation: US requirements and a broader view. Water Sci Technol. 40 (9), 63-70, 1999.
[34] S. Lee and J. Park. Identification of Dissolved Organic Matter Origin Using Molecular Level Analysis Methods. Water-Sui. 14 (9), 2022.
[35] S.P. Gorde and M.V. Jadhav. Assessment of water quality parameters: a review. International Journal of Engineering Research and Applications 3(36), 2029-2035, 2013.
[36] A. Marandi, M. Polikarpus and A. Joeleht. A new approach for describing the relationship between electrical conductivity and major anion concentration in natural waters. Appl Geochem. 38, 103-109, 2013.
[37] C.L. Tang, Z.Q. Zhang and X.N. Sun. Effect of common ions on nitrate removal by zero-valent iron from alkaline soil. J Hazard Mater. 231, 114-119, 2012.
[38] M.A. Sanchez-Monedero, A. Roig, C. Paredes and M.P. Bernal. Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. Bioresource Technol. 78 (3), 301-308, 2001.
[39] N. Akhtar, M.I.S. Ishak, S.A. Bhawani and K. Umar. Various Natural and Anthropogenic Factors Responsible for Water Quality Degradation: A Review. Water-Sui. 13 (19), 2021.
[40] R. Bhateria and D. Jain. Water quality assessment of lake water: a review. Sust Wat Resour Man. 2 (2), 161-173, 2016.
[41] N. Khatri and S. Tyagi. Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas. Front Life Sci. 8 (1), 23-39, 2015.
[42] G.S. Bilotta and R.E. Brazier. Understanding the influence of suspended solids on water quality and aquatic biota. Water Res. 42 (12), 2849-2861, 2008.