An investigation of inorganic chemicals and heavy metals in Kırklareli Dam water, Thrace region

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ABSTRACT

This study provides a baseline for the assessment of the inorganic pollution, especially metal contamination, in the waters of the Kırklareli dam on the Ergene River basin. A survey of inorganic chemicals was performed in water samples collected from the Kırklareli dam reservoirs in 2014–2015. Water samples from five sampling sites were collected and analyzed for 12 different water quality parameters. Using these data, regional irrigation water quality was assessed via a method prescribed by the United States Department of Agriculture (USDA). Results from the application of this method indicated that the salinity of the dam water, as represented by electrical conductivity (ECw), was at a medium level (C2: 250–750 micromhos cm⁻¹), and that the sodium adsorption ratio (SAR) ranged from medium (S2: 10–18) to high (S3: 18–26) sodicity. Therefore, the dam water from the sampling sites of 1, 3, 4, and 5 was predominantly of the C2–S2 class. Cation concentrations were found to be higher in January than in the other months. In examining the water quality classes in terms of measured physico-chemical parameters, the dam water was determined to be class I for pH, EC, TSS and cations. Furthermore, the results showed that the Pb concentrations in the Kırklareli dam water (10–200 µg L⁻¹) were of the class IV quality, which is the maximum limit of the Turkish Water Pollution Control Regulations. The Fe and Mn concentrations in the dam water were class II.

Keywords: Dam waters quality; Heavy metals; Hydrochemistry; Inorganic chemicals, Irrigation water

1. Introduction

Water pollution and scarcity are the most important anthropogenic causes of global change in aquatic ecosystems. Surface waters are key potential sources of irrigation water. In many areas of the world, especially arid and semiarid regions, irrigated agriculture is essential for achieving targeted production.

Lakes are critical resources for the preservation of fresh water and the replenishment of underground water, and they also play a key role in regulating local climates and improving the environment; consequently, they are considered to be one of the most versatile ecosystems in the world [1].

Surface water, which is more susceptible to contamination, is often used for irrigation. In some regions, in the face of a shortage of fresh water, reclaimed wastewater is used for agricultural purposes in an effort to conserve hydrological resources [2]. The suitability of water for irrigation purposes is determined through chemical analysis. Irrigation agriculture depends on adequate water supplies of usable quality. Chemical impurities can be harmful when present above certain fairly well-defined limits. The main soluble constituents in water are the cations Ca, Mg, and Na and are of prime importance in determining the quality of irrigation water and its suitability for irrigation purposes. When there is intensive use of nearly all good quality water supplies, plans for new irrigation projects and additional supplies are limited to the use of lower quality and less desirable sources, which means that proper designs must be made for environmental management [3].

Sodium content is the ratio of sodium concentration to the concentrations of calcium and magnesium (beneficial

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elements), otherwise known as the sodium adsorption ratio (SAR). High levels of soil salinity and SAR cause deterioration of soil structure, decrease of soil permeability and reduction of crop yields due to toxic and osmotic effects [4].

Among the numerous contaminants defiling aquatic environments, pollution by heavy metals is a major concern and has become a global phenomenon on account of the metals' toxicity, decades-long life-span, bioaccumulation and biomagnifications in the food chain. Heavy metals are usually present at low concentrations in aquatic ecosystems, but deposits of anthropogenic origin have raised the concentrations of heavy metals, creating environmental problems in coastal zones, lakes and rivers [5-6]. These heavy metals affect environmental quality by accumulating in reservoirs and can result in serious human health hazards [7]. The chemical speciation of heavy metals has been of particular interest, insofar as their toxicities, bioavailability, pathways of transportation and other properties depend to a great extent on their species. Additionally, the composition of heavy metal species in water sources is a good indicator of the presence of anthropogenic contamination [8].

Large-scale emissions of and contaminations by heavy metals are of particular concern at present in Asian developing nations because of the rapid economic development in that region and the recent population growth [9].

Surface water has both organic and inorganic based pollution related to uncontrolled agricultural and industrial activities. There have been many research projects on irrigation water and assessments of inorganic chemicals in surface waters, including those conducted in South China [10], Lahore, Pakistan [11], Spain [12,13], Benin [14], and the Jilh aquifer in Saudi Arabia [15]. Furthermore, numerous studies have been conducted on the presence of heavy metals in surface waters and/or of sediments in coastal zones, rivers and lakes, such as Lake Brullus in Egypt [16], Izmit Bay in Turkey [17], the Maas, Rijn, the Waal and IJssel River in Holland [18], the Pyeongchang River in Korea [6], Istanbul Strait in Turkey [19] and the Guangdong Coast in China [20].

According to Demirezen et al. [21] in populated areas, metals such as Cd, Cu, Cr, Ni and Pb are released into the environment by a number of industries (e.g., the automotive, metal-producing, electroplating, and battery and electric cable manufacturing, mining, tannery, steel and textile industries).

Very few studies have focused on the Ergene River basin, where the Kırklareli dam is located, especially regarding the subject of inorganic pollution [22–24]. Surface and ground waters in the basin are constantly subject to pollution caused by the rapid increase in population and the intensity of agricultural and industrial activities. Monitoring of dam water is necessary for determining the levels of contamination in irrigation and drinking water. Further research on the heavy metals assessment and the physico-chemical properties is needed to reveal the contamination profile in the basin.

The present study aims to:

- 1. Investigate the seasonal changes in physicochemical properties (pH, EC, TSS, SAR) of Kırklareli dam.
- 2. Determine the concentration and distribution of certain metals (Ca, Mg, Na, Fe, Mn, Cu, Zn and Pb) in

the water and determine the suitability for irrigation and drinking water.

2. Methods and materials

2.1. *Study area*

Kırklareli is located on the north of the Ergene River basin in the northwest part of Turkey. It is one of three provinces located in the Thrace Region. Being the largest city in the north section of the Ergene River basin, Kırklareli plays a key role, not only in water storage, agricultural irrigation, water supply and climatic regulation, but also in producing a good deal of marketable grain and freshwater fish. One of the main activities in the city is agriculture, with cereals, sunflower, sugar beet, pulses, corn, and forage crops being the main agricultural products cultivated [25].

The surface water potential of Kırklareli province is 1137 hm³, which constitutes 1.2% of the country's surface water, and the amount of economically irrigable lands within the province is 112,013 ha. Kırklareli dam is one of the most important reservoirs in the Thrace Region. The dam supplies both the drinking water and the irrigation water to the province. Located on the eytandere stream, the dam was constructed between 1985 and 1995 for irrigation, flood control, drinking water and industrial use water. The body volume of the dam is 1,838,000 m³, while the area of the lake is 6,5 km². The average height from the riverbed of eytandere stream is 71 m, and the stream provides water for an area of 9050 ha. Major land use in the common watershed of the lake is agriculture and settlements. Because of rapid industrial development in the Thrace Region, heavy metal pollution is common. The Kırklareli Organized Industrial Zone largely consists of textile factories, and white goods, glass, oil, food, and chemical factories [26]. These factories located in the basin discharge their waste into the Ergene Basin and its branches. As a result of these activities as well as population growth, the level of contamination has substantially increased. Therefore, the environmental quality in the aquatic system of the Kırklareli dam has direct and significant effects on the quality of the city's drinking water and on the stability and biodiversity of the aquatic ecosystem.

2.2. Sampling and sample preparation

The samples were taken from five sampling stations on the Kırklareli dam in compliance with the Turkish Water Pollution Control Regulation Sampling and Analysis Methods Notification [27]. Seasonal water samples were taken from stations designated as 1, 2, 3, 4, and 5 (Fig. 1) and from the surface layer of the dam. In particular, these samples were taken from parts of the dam reserved for irrigation water (stations 1, 3), from a dirty/polluted part (station 2) and from relatively cleaner parts (stations 4 and 5). March and July samples were taken in 2014, while January samples were taken in 2015. Samples were placed in acid-rinsed polyethylene containers before immediately being taken to the laboratory. Field water sampling and measurements were conducted according to standard methods [28]. All of the chemicals used were of the highest purity available



Fig. 1. Map of Kırklareli dam and selected stations (1-5).

(Merck), and all of the glassware and laboratory equipment used were carefully cleaned with HCl to minimize potential contamination.

Water samples were collected in 500 mL bottles for determination of metals and in 1 L bottles for calculation of physicochemical parameters. The samples were stored at +4°C until they underwent analysis. This analysis focused on four physicochemical parameters: pH, electrical conductivity, total suspended solids and seven metals (Ca, Mg, Na, Fe, Mn, Cu, Zn and Pb).

At the laboratory, the water samples where filtered. Electrical conductivity (EC_w) and pH of the samples were measured directly after collection and then monitored using a multi-parameter measurement instrument (Thermo Orion 3 star) after performing appropriate calibrations with standard buffer solutions. Concentrations of TSS were measured using the standard drying method at 103–105°C [28].

Metals were measured using ICP-OES in the laboratory of the Atatürk Research Institute of Soil, Water and Agricultural Meteorology in Kırklareli. Metal samples were filtered immediately after transporting them to the laboratory (0.45 µm Millipore filter), and HNO₃ was added to the samples until they acquired a pH of 2. All metals were determined by direct aspiration of the sample solution into ICP-OES (Spectro Blue model). The USEPA Method, Method 3005A [29], and USEPA Method 200.2 inductively coupled plasma-optical emission spectrometry ICP-OES [30] were used, respectively, to digest and analyze Ca Mg, Na, Fe, Mn, Cu, Zn and Pb. Reagent and procedural blanks were determined in parallel with the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples. The analytical precision was within the range of ±10%. Accuracy of the analytical procedure was checked by analyzing the standard reference materials. Recovery rates ranged from 99% to 100% for all investigated elements.

The method prescribed by the United States Department of Agriculture (USDA) was used for water quality assessment [31]. The USDA method is primarily based on water electric conductivity (EC_w), which serves to indicate the total concentration of soluble salts in irrigation waters, usually expressed in micromhos cm⁻¹ at 25°C, and its sodium adsorption ratio (SAR). High SAR values are indication of sodium hazard (alkali hazard). The sodium adsorption ratio is expressed as:

$$SAR = \frac{Na}{\sqrt{Ca + Mg}}$$
(1)

where Na is the concentration of sodium ions (meq L^{-1}), Ca the concentration of calcium ions (meq L^{-1}), and Mg the concentration of magnesium ions (meq L^{-1}).

Physico-chemical parameters were compared according to the Turkish Irrigation Water Regulations [27], while concentrations of heavy metals were compared according to the Turkish Water Pollution Control Regulations [32], Water Intended for Human Consumption Standard (Council Directive 98/83/EC) [33], WHO [34] and USEPA [35].

2.3. Statistical analyses

Statistical analyses of data were performed using SPSS statistical software package (Version 10) [36].

3. Results and discussion

3.1. Physico-chemical parameters

The physico-chemical parameters from the sampling stations of the study area are shown in Fig. 2. The pH values ranged between 7.3 and 8.5 and were found to be generally lower in January compared to the other months, the results of which can be attributed to higher amounts of precipitation and inflow of freshwater from the rivers in January and the consequent dilution of the dam waters. Likewise, in inverse fashion, the pH rose in July due to a decrease in precipitation and reduced rate of river flow to the reservoir of the dam.

The TSS values ranged between 0.8 and 92 mg/L and were determined to be generally higher in July than in the other months at sampling station 2. During the winter, strong winds from the Black Sea, located north east of the dam area, blow in, dispersing solid matter throughout the dam water and clouding it.

The TSS values were generally higher at sampling station 2 than at the other sampling stations. As this particular sampling station was chosen from the agricultural areas, there was a greater amount of solid matter coming from the superficial flow.

In this study, the values of pH and TSS were within an acceptable range for irrigation and drinking water.

3.2. Distribution of Ca, Mg, Na, SAR and EC_m

The distribution of the Ca , Mg and Na cations are given in Fig. 3, where it can be seen that the cation concentrations were generally higher in July than in the other months. High evaporation and increasing anthropogenic activities, such as those related to agricultural enterprises, in the summer elevated the total concentrations of metals.



Fig. 2. Physico-chemical parameters, at the sampling stations from the study area, during 2014–2015. Sampling stations: 1, 2,

3, 4, 5.



Fig. 3. Cross section of sodium, calcium, magnesium of the sampling stations: 1, 2, 3, 4, 5.

The Ca concentration (1.48–33.79 meq L⁻¹) was higher at station 1 than at the other stations. The Mg concentrations ranged from 0.05 to 11.66 meq L⁻¹ and the Na concentrations from 0.36 to 9.29 meq L⁻¹. Sodium, magnesium and calcium contents were within an acceptable range for irrigation water.

The SAR contours ranged from 1.9 to 3.8 (Fig. 4a). A hazardous SAR tends to result in the breakdown of the soil structure and leads to dispersion and decreased water permeability. The dam waters demonstrated suitability for all kinds of cultivation of plants sensitive to sodium. These results obtained were similar to the work done by many researchers [37–39].

The areal distribution of ECw at 25°C for dissolved salts in the dam water ranged from 265 to 325 micromhos cm⁻¹ (Fig. 4b). According to the Turkish Irrigation Water Regulations [27], the dam water was determined to be good (class II) at the 1, 2, 3, 4, and 5 sampling stations. The EC_w was



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Fig. 4. Cross section of (a) SAR of the sampling stations; (b) EC_w of the sampling stations: 1, 2, 3, 4, 5.

below 400 micromhos cm⁻¹ at all sampling stations. The results showed that the ECw of Kırklareli dam was within quality class I, which is the limit of the Turkish Water Pollution Control Regulations [32].

3.3. Classifications of the Kırklareli dam water for irrigation

The areal distribution of cations and other irrigation water quality assessment components have already been discussed. In order to secure a simple technique appropriate to describe the suitability of dam waters for irrigation, the distribution of the major cations in the aquifer were subjected to the USDA classification techniques [31].

3.4. Classification according to USDA method

The USDA classification for salinity (C) and sodicity hazards (S) in the Kırklareli dam are shown in Fig. 5. Most of the sampling stations within the low salinity hazard zone were in the S1 class. According to the USDA classification system, the water from the dam in terms of the salinity class was C2, which is of a medium quality for irrigation waters. The sodium adsorption ratio (SAR) ranged from medium (S2) to high (S3) sodicity. Similar results were reported by Akinyemi and Souley [3].

The combined ECw/SAR classification of the dam water was C2–S2 (good/class II) at the sampling stations of 1, 3, 4, and 5, while it was C2–S3 (usable/class III) at sampling station 2 according to the USDA classification system [31].

3.5. Distribution of Fe, Mn, Cu, Zn, Pb

The distribution of the iron, manganese, copper, zinc and lead metals is shown in Table 1. The concentrations of heavy metals were generally higher at sampling stations 1



Fig. 5. Classification of water in the Kırklareli dam based on the USDA method.

and 3 than at the other sampling stations. The difference in the distribution of heavy metals at the five stations can be attributed to the inflow of freshwater from the rivers, anthropogenic wastes from the mines, which was the source point for the flow of heavy metals into the dam water, and the transport of industrial wastes towards the dam by water currents. Precipitation and seasonal anthropogenic activities, therefore, played important roles in the spread of heavy metals in the surface water of the reservoirs [40].

The Fe concentrations ranged from 70 to 2200 μ g L⁻¹, Mn concentrations ranged from 100 to 800 μ g L⁻¹, and Cu concentrations ranged from 10 to 30 μ g L⁻¹. The Fe and Mn concentrations indicated that the dam was class II according to the limit values prescribed by the Turkish Water Pollution Control Regulations [32], and these concentrations were very high according to the Water Intended for Human Consumption Standard (Council Directive 98/83/EC) [33]. The Pb concentrations ranged from 10 to 200 μ g L⁻¹, indicating that the dam water was of class IV quality for Pb (10–200 μ g L⁻¹). Similar results were found in other studies [41,42].

The amount of heavy metals was determined, in decreasing order, by month, to be: Fe>Pb>Cu>Zn>Mn in March, Fe>Pb>Zn>Mn>Cu> in July and Fe>Pb>Mn>Cu> Zn in January.

In comparing the concentrations determined from the present study and those presented in the literature, it was concluded that the concentrations observed in the Kırklareli dam were either lower or higher than those that have been previously recorded (Table 2).

The results of correlation analysis are shown in Table 3, where it can be seen that there was a positive correlation between iron and calcium, EC and Mn, and Pb and Na, while there was a negative correlation between iron, calcium and pH. This negative correlation can be attributed to the solubility of these metals. Decreased pH might have also enhanced the solubility and mobility of metals, the results of which increase their presence [47].

Table 1

Cross section of iron, manganese, copper, zinc and lead of the sampling stations: 1, 2, 3, 4, 5

Station	Coordinates	Seasons*	Fe	Mn	Cu	Zn	Pb
Number			µg L-	µg L⁻¹	µg L-₁	µg L-₁	µg L-
		March	1000	100	30	10	200
1	414209 N	July	2200	400	10	120	70
	271232E	January	1100	800	20	20	150
		March	1200	100	30	10	80
2	414423 N	July	700	500	10	70	50
	271647 E	January	1000	600	20	30	100
		March	1300	800	20	70	40
3	414447 N	July	600	800	10	100	20
	271507 E	January	1000	700	20	40	80
		March	50	100	10	10	10
4	414539 N	July	90	200	10	10	40
	271644 E	January	70	600	10	120	70
		March	2000	100	20	10	110
5	414546 N	July	90	200	10	10	40
	271724 E	January	80	600	20	20	80

*March and July were in 2014, January was in 2015.

Table 2

Maximum concentrations of heavy metals in the Kırklareli dam reservoir, and comparison with other studies and guidelines (MCL)

	Heavy metals					
	Fe	Mn	Cu	Zn	Pb	
This study (µg L ⁻¹)	2200	800	30	120	200	
Hough Park Lake (µg L ⁻¹)ª	298	93	1	3	0.4	
Burullus Lake (µg L ⁻¹⁾ b	3000	nd	50	125	5000	
Qattieneh Lake (µg L ⁻¹)°	nd	nd	12	59	10	
Dicle Dam (µg L ⁻¹) ^d	189.24	nd	9.63	3.62	22.03	
Atatürk Dam (ppm) ^e	19.265	514.07	22.70	64	nd	
Turkish Environmental Guidelines						
Class I	<300	100	20	200	10	
Class II	1000	500	50	500	20	
Class III	5000	3000	200	2000	50	
Class IV	>5000	>3000	>200	>2000	>50	
Water quality criteria for drinking water						
EC (1998), (µg L ⁻¹)	200	500	2000	1000	10	
WHO (2004), (µg L ⁻¹)	300	500	2000	5000	10	
USEPA (2009), (µg L ⁻¹)	300	500	1300	5000	15	
^a [43], ^b [44], ^c [45], ^d [40], ^e [46]						

Table 3

Correlations matrix for heavy metal concentrations and the physicochemical parameters in dam waters

	pН	EC	TSS	SAR	Ca	Mg	Na	Fe	Mn	Cu	Zn	Pb
pН	1											
EC	-0.83	1										
TSS	0.43	-0.16	1									
SAR	0.62	-0.22	0.73	1								
Ca	-0.98**	0.87	-0.38	-0.63	1							
Mg	-0.24	-0.09	-0.88	-0.84	0.24	1						
Na	0.71	-0.49	-0.12	0.50	-0.74	0.03	1					
Fe	-0.94^{*}	0.84	-0.63	-0.63	0.93*	0.39	-0.47	1				
Mn	-0.85	0.96**	-0.19	-0.17	0.85	-0.14	-0.46	-0.39	1			
Cu	-0.32	0.30	0.54	0.51	-0.55	0.38	0.87	0.28	-0.13	1		
Zn	0.52	-0.59	-0.07	0.43	-0.65	-0.09	0.69	-0.39	-0.39	-0.11	1	
Pb	0.75	-0.45	0.10	0.69	-0.77	-0.22	0.96**	-0.41	-0.41	0.74	0.69	1

Bold values are significant. * Correlation is significant at the 0.05 level, ** Correlation is significant at the 0.01 level.

4. Conclusion

The obtained results have shown that Fe, Mn, and Pbare the most abundant elements in the reservoirs, with lesser amounts of Zn and Cu present. During the study period, the heavy metals analyzed did not show statistically significant spatial variations. TSS, pH, EC, SAR and cation contents are within an acceptable range for irrigation water, and have been determined to be of class I surface water quality. When compared against the drinking water quality guidelines established by EC, WHO and USEPA, Fe, Mn and Pb have been determined to be potential pollutants in the dam reservoirs and may therefore pose health risks for the residents in the region. Anthropogenic activities are the main sources of heavy metals, and identification of contamination factors have indicated that Fe, Mn and Pb pollution area serious threatfor the study area. In order to track immediate discharges, the water quality of the dam should be monitored regularly within short intervals of time.

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