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ERZİNCAN
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ERZİNCAN - TÜRKİYE

ERZİNCAN ÜNİVERSİTESİ
ULUSLARARASI ERZİNCAN SEMPOZYUMU
28 EYLÜL – 1 EKİM 2016 ERZİNCAN
BİLDİRİLER
CİLT 3

EDİTÖR
Yrd. Doç. Dr. Hüsrev AKIN

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INVESTIGATION OF THE QUALITY OF NATURAL WATER RESOURCES IN THE REGION OF ERZINCAN

ERZİNCAN BÖLGESİNDEKİ DOĞAL SU KAYNAKLARININ KALİTESİNİN

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Abstract

Nowadays, the amount of natural and clean waters for each person is decreasing due to some reasons such as rapidly developing industrialization, excessive growth of the human population and environmental pollution. The available water resources in the earth varies from one region to others and do not disperse proportionally. Therefore, in the future years, a major water problem will occur in the world. Because of all these reasons, all states in the world must show a vital struggle to meet the water needs adequately and safely. Although there is enough natural and clean water resources in our country, these resources cannot be utilized appropriately.

In this study, the quality of water samples which were collected from the Erzincan region (Karasu River, Kadi Lake, Erzincan Dam Lake, Tercan Dam Lake, and Böğert-Ekşisu) were investigated. Some analytical parameters such as pH and temperature were determined by measuring at the collected locations. Total water hardness (French hardness, in mg CaCO₃/100 mL of water), the amount of various anions (CO₃²⁻, HCO₃⁻, SO₄²⁻ and Cl⁻), metal, and non-toxic metals ions (Na⁺, K⁺, Mg²⁺, As³⁺, Pb²⁺, Hg²⁺ etc.) were tested by using various analytical and spectroscopic techniques. When the obtained results were compared to standard values of Turkish Standards Institution (TSE), the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA/USA), it was observed that they were in accordance with the standards.

Key words: Erzincan Water Resources, Hardness, pH, Cation-Anion Analysis.

1. Introduction

Water is necessary for the survival and staying healthy of human being, it also has importance for the many different sectors of economy. However, water resources is scattered irregularly in terms of time and place. Natural water on earth can be in the air, on the ground or underground. Fresh water constitutes 2.5% part of all the water on earth and most of it is frozen in icecaps. The rest of this fresh water is underground water, only a little part of it is on the ground or in the air. Average amount of water per capita varies for example it is less than 50 m³ in some part of the Middle East and in some moist and sparsely populated areas it is more than 100.000 m³. United Nations created a database in decades for each country about its prediction of their water consumption. Although this database is a general reference means, it also has some disadvantages. Numbers only show the present maximum amount theoretically and it can be redundantly predicted. Also, annual and national averages may hide local and seasonal differences [1-2].

In the worldwide, water resources face to serious threats caused by people's activities and natural events. These include environmental pollution, climate change, urban growth and destruction of forests. Each of them often has a direct effect on ecosystems namely on water resources. Although the water conscious about a better control and protection of water has increased in last decade, economic criteria and political thinking have tendency to use water in

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every level. Also, desired opportunities are not given to scientific and technological applications [1-2].

Negative pressure on water resources have increased due to people's activities such as urbanization, population growth, increasing living standards, increasing competition for water and pollution. All of them have become much more severe with climate change and changes in natural conditions. However, some advancement about appreciating the water resources is also recorded. Authorities have started to evaluate the water amount and quality together and coordinate some administrative efforts to use the water resources correctly [1-2].

Low quality of water and using the water resources insensibly may limit a country's economic development, give damage to health and affect means of living. It must be paid attention to enhance present natural resources and decrease the demand and loss while managing water resources [1-2].

Especially, water resources of our country are under great threats. More reliable information related to present amount and quality of water and how this presence changes in time and in different areas is needed. People's activities affect the presence and quality of water in many ways. Some regulations are needed to manage the water resources more responsibly and constantly [1-2].

In this study, the quality of water samples which were collected from the Erzincan region (Karasu River, Kadı Lake, Erzincan Dam Lake, Tercan Dam Lake, and Böğert-Ekşisu) were investigated. Some analytical parameters such as pH and temperature were determined by measuring at the collected locations. Total water hardness (French hardness, in mg CaCO_3 /100 mL of water), the amount of various anions (CO_3^{2-} , HCO_3^- , SO_4^{2-} and Cl^-), metal, and non-toxic metals ions (Na^+ , K^+ , Mg^{2+} , As^{3+} , Pb^{2+} , Hg^{2+} etc.) were tested by using various analytical and spectroscopic techniques. When the obtained results were compared to standard values of Turkish Standards Institution (TSE), the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA/USA), it was observed that they were in accordance with the standards.

2. Material and Method

2.1. Apparatus and chemicals

Analyses of the samples with analytical and spectroscopic techniques were done in Ege University, Faculty of Sciences. All the glass materials used in analyses were calibrated in laboratory temperature. Chemicals used in the analyses such as Na_2CO_3 , HCl , NaOH , NH_3 , AgNO_3 , ethylene di amine tetra acetic acid (EDTA), NaCl etc. were obtained from MERCK firm. All the used chemicals were in analytical grade and no extra purification process were carried out. Also, used indicators were obtained from FLUKA firm. Analyses of the some anions were done via volumetric methods. Cation analyses were done according to EPA-375 standards in Ege University, Center of Drug Research and Development Laboratories using plasm-mass spectrometer (ICP-MS) Agilent 7500 device.

2.2. Methods

2.2.1. Volumetric CO_3^{2-} and HCO_3^- analyses:

In this method, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in drinking water are analyzed volumetrically. Firstly, before starting the analysis HCl solution was adjusted as suggested in the literature. In the adjustment, Na_2CO_3 which is primary standard and in fixed weighing in 107°C was used. Phenol phthalein and methyl orange indicators and CO_3^{2-} and HCO_3^- in water samples were analyzed volumetrically with adjusted HCl solution [3-5].

2.2.2. Hardness determination:

Hardness is an important parameter in drinking water. Hard water prevents water from frothing. Therefore, hardness of water should be measure in terms of quality of drinking water.

In this study, total hardness of water was measured by volumetric method. For this purpose, 0.01 M EDTA solution was prepared. This solution was adjusted by using standard calcium solution. Eriochrome Black T (EBT) indicator was prepared in 67% ethyl alcohol solution. Buffer solution was prepared by mixing (67.5 g) ammonium chloride and (570 mL) concentrated ammoniac. 1 mL 0.01 M EDTA is equal to 1 mg CaCO_3 . Results were calculated as being equal to calcium carbonate in 100 mL water and given as French hardness [6-8].

Calculated results are given in below;

Total Hardness = $V_1 \times 4$ (V_1 : Volume of spent EDTA solution)

Permanent Hardness = $V_2 \times 2$ (V_2 : Volume of spent EDTA solution)

Temporary Hardness = Total Hardness - Permanent Hardness

2.2.3. Cl^- (Chloride) determination:

Determination of chloride ions in drinking water samples were made by titration of chloride ions with AgNO_3 . No adjustments were done as silver nitrate is pure and its solutions are stable in the dark [3-7].

2.2.4. Cation analyses:

Analyses of the cations in water samples were carried out by inductively coupled plasma-mass spectrometer (ICP-MS). ICP-MS provides opportunity to measure qualitatively and quantitatively many elements faster, cheaper, sensitive and accurate. Concentration of all the elements in water samples can be measured in a very short time. Liquid samples in ICP-MS measurement technique can be measured with "Solution ICP-MS" technique and solid samples can also be measured in solution. Recently, many toxic and heavy metals can be determined with this method in ng/mL level [8-12].

3. Results

Analysis results of the water samples collected from natural water resources in Erzincan region (Karasu River, Kadı Lake in Kemaliye, Erzincan Dam Lake, Tercan Dam Lake and Böğert-Ekşisu water) by using analytical and spectroscopic techniques was given below.

3.1. Temperature and pH analyses of water samples:

Temperature has a great effect on all the vital activity such as their respiration, food consumption and digestion of aquatic organisms [5,13-14]. Water temperatures where water samples were collected vary 8-24°C. These values are compatible with TSE 266, WHO and EPA/USA standards. Necessary optimum limits of pH, which is a crucial parameter in biological and chemical systems of natural water, is 8.50-9.00 for aquatic organisms [5]. pH range for drinking water is between 6.50-8.50. As a result of the water samples analyses it is concluded that pH range varies between 8.00-8.55. Only pH of the Böğert-Ekşisu sample is 5.87 and this value is normal as Böğert-Ekşisu is natural mineral water. It outcrops with its all minerals and carbon dioxide from the underground cracks. Therefore, it is an expected situation that its acid is very much due to decomposed carbon dioxide. These values are compatible with WHO, EPA/USA and TSE 266 criteria. The determined values of temperature and pH of water samples are given in Table 1.

Table 1. Values of temperature and pH of water samples.

Determined Parameter	Collected area of samples *					Drinking water standards		
	Erzincan Dam Lake	Kemaliye Kadı Lake	Tercan Dam Lake	Karasu River Water	Böğert- Ekşisu Water	TSE, mg/L	WHO, mg/L	EPA/USA, mg/L

	23	08	24	17	16			
Temperature, °C	23	09	24	16	17	12-25	–	–
	8	12	25	17	17			
	8.51	8.05	8.47	8.47	5.83			
pH	8.50	8.07	8.51	8.50	5.99	6.50-9.20	6.50-9.50	6.50-8.50
	8.30	8.15	8.55	8.63	5.80			

* Three different samples were taken from each region.

3.2. Determination of CO_3^{2-} and HCO_3^- ions in water samples:

Generally, amount of hydroxide, carbonate and bicarbonate form the alkalinity (base) of water. Alkalinity is determined by phenol phthalein and methyl orange indicators. The obtained results help find the amount of carbonate and bicarbonate of water [15-16]. Carbonate and bicarbonate values obtained as a result of water sample analyses is shown in Table 2. As it can be seen from the results, HCO_3^- amount of Böğert-Ekşisu mineral water sample is higher than the others. The result of it is that Böğert-Ekşisu is a natural mineral water spring.

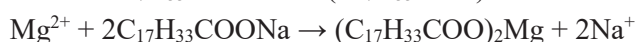
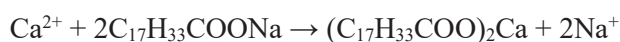
Table 2. The determined amounts of carbonate and bicarbonate in water samples.

Collected area of sample	* CO_3^{2-} , (mg/L)	HCO_3^- , (mg/L)
Erzincan dam lake	-	133.95
Kemaliye kadı lake	-	151.52
Tercan dam lake	-	127.36
Karasu river water	-	164.70
Böğert-Ekşisu water	-	394.16

* The results could not be determined as the volumetric because they are below the 10 mg/L value.

3.3. Total hardness degree of water samples:

Hardness in the water comes from dissolved calcium (Ca) and magnesium (Mg) salts. Hardness of the water can also be explained as the soap decomposition capacity of water. Ca^{2+} and Mg^{2+} ions in hard water react with soap and create the calcium and magnesium soap which cannot be dissolve in the water.



Hardness can be described as total concentration of calcium and magnesium ions from type of calcium carbonate. It can also include the other ions that increase the hardness of water. Water can be shown with various hardness degree units [17-18]. The most commonly used of hardness degree units are shown in Table 3. In this study, it was found as a result of the water samples analyses that Erzincan Dam lake has the lowest hardness degree (16 °F) and Böğert-Ekşisu has the highest one (36 °F). These values are the highest according to standards and they are in hard water group.

Table 3. Various hardness values of the waters.

Hardness Unit	Symbol	Definition
German hardness	°dH	1 °dH= 10 mg CaO/1 L water
French hardness	°F	1 °F= 10 mg CaCO_3 /1 L water

British hardness	°e	1 °e= 10 mg CaCO ₃ /0.7 L water
Parts per million	ppm	1 ppm= 1 mg tuz/1 L water

Ca, Mg and total hardness values obtained as a result of the analyses of water samples collected from Erzincan region are shown in Table 4. Total hardness of the water samples are given as French hardness (mg CaCO₃/100 mL water). When obtained results and pH values of the water are compared, it is seen that the results are compatible with what is expected.

Table 4. Ca, Mg and total hardness values of water samples collected from various natural water resources in the region of erzincan

Determined Element	Collected area of samples					Drinking water standards		
	Erzincan Dam Lake	Kemaliye Kadı Lake	Tercan Dam Lake	Karasu River Water	Bögert-Ekşisu Water	TSE, mg/L	WHO, mg/L	EPA/USA, mg/L
Ca	15.86	32.14	30.79	36.08	34.77	100-200	-	-
Mg	13.83	7.20	8.53	13.28	62.15	30-50	30-50	-
Total Hardness *	16.00	24.00	22.00	24.00	36.00	-	-	-

* French hardness (mg CaCO₃/100 mL water)

3.4. Determination of Cl⁻ (Chloride) ions in water samples:

Chloride (Cl⁻) is known as the most common halide ion in nature. It is very commonly found ion in all natural and used water. Chloride gives damage to water network, water heater, washing machine and dish-washers. Kidney and higher tension problems may occur in case of drinking water with high chloride ions constantly. Also, it is one of the parameters that must be measured regularly. If it increases, then sea contribution or industrial pollution should be taken into consideration.

Chloride can be in water as compounds; NaCl, CaCl₂ or MgCl₂. It can also enter to underground water with dissolution or salty and fresh water inflow. If chloride concentration is with Ca²⁺ and Mg²⁺ cations, it does not create a salty taste in 1000 mg/L water. Chloride amount is much higher in used water than drinking water. Water with high chloride gives damage to metallic pipes and constructions [6]. In the study, chloride amount of water samples were analyzed by using argentometric method. The obtained results are shown in Table 5.

Table 5. The amount of chloride of water samples.

Determined Element	Collected area of samples					Drinking water standards		
	Erzincan Dam Lake	Kemaliye Kadı Lake	Tercan Dam Lake	Karasu River Water	Bögert-Ekşisu Water	TSE, mg/L	WHO, mg/L	EPA/USA, mg/L
Chloride	5.68	1.70	17.58	21.14	27.18	30	250	-

3.5. Determination of cation amounts in water samples:

As metals are normally present in rock and mine ore it is normal that they are also in organisms, sediments and soil [10]. As a result of people's activities and processes such as removal and opacity of rocks, amount of heavy metal in sea and lake depth increases in time. Metals that can be dissolved in water are much more intense in sediments and especially in large parts where rivers meet lakes and seas [19]. The determined amounts of cations in water samples are given as ppm (mg/L) in Table 6.

Table 6. Determined amounts of cations in water samples.

Determined Element	Collected area of samples					Drinking water standards		
	Erzincan Dam Lake	Kemaliye Kadi Lake	Tercan Dam Lake	Karasu River Water	Bögert-Ekşisu Water	TSE, mg/L	WHO, mg/L	EPA / USA, mg/L
Na	3.68	0.70	14.48	20.14	23.12	20-175	200	-
Mg	13.83	7.20	8.53	13.28	62.15	30-50	30-50	-
K	2.29	0.25	1.61	1.56	2.48	12	-	-
Ca	15.86	32.14	30.79	36.08	34.77	100-200	-	-
Fe	0.14	0.07	0.10	0.18	0.15	0.30	0.30	0.30
Mn	0.001	0.0003	0.06	0.02	0.19	0.10	0.10	0.05
Co	0.02	-*	0.23	1.94	0.13	-	-	-
Cu	1.11	0.93	2.00	1.27	0.23	1.00	1.00	1.00
Zn	0.02	0.03	0.02	0.17	0.02	5.00	5.00	5.00
B	0.51	0.02	0.02	0.02	-*	0.1-0.3	0.3	-

* Not measurable level.

3.6. Determination of some toxic metals in water samples:

Even if they are present in low concentrations in water, toxic substances can be cause diseases by damaging to human health and even death. The most important of these substances are given in below:

As, Cd, Hg, Ni, Pb, Sb, Se, Ag, V, and Cr

Many of these substances are present in the heavy metal group [10,19-22]. The determination of some toxic metals in water samples are shown in Table 7.

Table 7. The results of analysis of some toxic substances in water samples.

Determined Element	Collected area of samples					Permitted values of some toxic substances		
	Erzincan Dam Lake	Kemaliye Kadi Lake	Tercan Dam Lake	Karasu River Water	Bögert-Ekşisu Water	TSE, mg/L	WHO, mg/L	EPA/USA, mg/L
Ba	6.39	41.22	26.68	29.79	10.98	0.30	0.70	2.00
V	1.75	0.48	319	2.16	0.07	-	-	-
Cr	2.44	3.98	0.77	2.50	1.12	0.05	-	0.1
Ni	3.11	1.41	2.58	8.59	0.77	0.05	0.02	-
As	0.70	0.59	3.72	3.37	0.48	0.05	0.05	0.05
Se	0.90	0.83	1.13	1.08	1.64	0.01	0.04	0.05
Sb	0.01	0.01	0.03	0.03	0.03	0.01	0.004	0.006
Hg	0.06	-*	0.01	0.08	0.06	0.001	0.001	-
Pb	0.39	3.33	0.95	1.43	0.40	0.05	0.05	-

4. Discussion

The amount of natural and clean waters for each person has been decreasing recently due to some reasons such as rapidly developing industrialization, excessive growth of the human population and environmental pollution. The available water resources in the earth varies from one region to others and do not disperse proportionally. Therefore, in the future years, a major water problem will occur in the world. Because of all these reasons, all states in the world must show a vital struggle to meet the water needs adequately and safely.

The total amount of consumed fresh water in the world is 3.8 billion liters in one year. Approximately 70% of this amount in agriculture, 20% in industry, and 10% in daily household needs is used. The usage in food and beverage consumption includes a considerable amount in total usage of fresh water. Although there is enough natural and clean water resources in our country, these resources cannot be utilized appropriately.

As a results, in this study which was supported by the Office of Scientific Research Projects, Erzincan University, the quality of water samples which were collected from the Erzincan region (Karasu River, Kadı Lake, Erzincan Dam Lake, Tercan Dam Lake, and Böğert-Ekşisu) were investigated. Some analytical parameters such as pH and temperature were determined by measuring at the collected locations. Total water hardness (French hardness, in mg CaCO₃/100 mL of water), the amount of various anions (CO₃²⁻, HCO₃⁻, SO₄²⁻ and Cl⁻), metal, and non-toxic metals ions (Na⁺, K⁺, Mg²⁺, As³⁺, Pb²⁺, Hg²⁺ etc.) were tested by using various analytical and spectroscopic techniques. When the obtained results were compared to standard values of Turkish Standards Institution (TSE), the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA/USA), it was observed that they were in accordance with the standards.

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