Araştırma Makalesi / Research Article

Seasonal Change of Heavy Metals' Levels in Surface Waters of Siirt Region

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Abstract
The rapid increase in the population of our country, the growing agricultural, industrial, and mining activities in recent years and the necessity to meet the needs of the growing population increase the demand for water rapidly. The increase in the need for water requires monitoring and control of surface clean water resources, which are limited, and determining priority water policies. For this reason, not only the water quality but also the amount of water resources is important. In this study, some heavy and metal determinations (As, Cu, Co, Ni, Cd, Cr, Mn, Pb) were performed in the major surface waters (Kezer, Başur, Bitlis, Botan and Zarova rivers) in Siirt region and seasonal changes were investigated. The amount of heavy metals determined as a result of this study is below the levels determined by WHO (World Health Organization), EPA (Environmental Protection Agency) and TSE (Turkısh Standard İnstitute). However, it was concluded that the levels of these heavy metals analyzed did not change significantly seasonally

Keywords: Siirt region, heavy metal, surface water, seasonal variation.

Siirt Bölgesi Yüzey Sularında Ağır Metal Seviyelerinin Mevsimsel Değişimi

Öz
Ülkemiz nüfusunun hızla artması, son yıllarda artan tarımsal, sanayi ve madencilik faaliyetleri artan nüfusun ihtiyaçlarının karşılanması gerekliliği su talebini hızla artırmaktadır. Su ihtiyacındaki artış, sınırlı olan yüzey temiz su kaynaklarının izlenmesi, kontrol edilmesini öncelikli su politikalarının belirlenmesini gerektirir. Bu nedenle sadece su kalitesi değil, aynı zamanda su kaynaklarının miktarı da önemlidir. Bu çalışmada Siirt bölgesindeki başlıca yüzey sularında (Kezer, Başur, Bitlis, Botan ve Zarova nehirleri) bazı ağır ve metal tespitleri (As, Cu, Co, Ni, Cd, Cr, Mn, Pb) yapılmış ve mevsimsel değişiklikler araştırılmıştır. Bu çalışma sonucunda belirlenen ağır metal miktarı WHO (Dünya Sağlık Örgütü), EPA (Çevre Koruma Ajansı) ve TSE (Türkiye Standart Enstitüsü) tarafından belirlenen seviyelerin altındadır. Bununla birlikte, analiz edilen bu ağır metallerin seviyelerinin mevsimsel olarak önemli ölçüde değişmediği sonucuna varılmıştır.

Anahtar kelimeler: Siirt bölgesi, ağır metal, yüzey suyu.

1. Introduction

Heavy metals are metallic elements whose atomic weight is more than 40 and whose electron distribution on its axis is similar, or elements whose specific gravity is more than 5 g/cm^3 [1]. Metals are carried into the waters by rock fragments carried by erosion, dust carried by the wind, volcanic activity, burning of forests and vegetation [2]. Heavy metals constitute the most important source of inorganic contamination in the waters. Some heavy metals are required to live in appropriate concentrations and their deficiencies produce a variety of symptomatic disorders. Heavy metals are potentially toxic to organisms at high concentrations, whether necessary or not [3]. Metals that pollute water can be reflected naturally from soil to water sources, and they can also pollute water through industrial, urban and agricultural wastes. The main metals that pollute water and pass from soil to water are Na, K, Ca, Mg, Bi, Sb, Fe and partly Al. Toxic metals that pollute water through industrial and

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domestic wastes are metals such as Al, Pb, Cd, Ni, Cu, Hg, As, Fr, Co, Mn and Zn. The most dangerous ones are Hg, Cd, Bi, Sb, Pb and As [4].

Of these metals, arsenic is one of the 20 most commonly found elements in the Earth's crust. It is in the range of 1.5-2mg/l in the Earth's crust. The main way of spreading and transporting arsenic to the environment is water [5]. Arsenic is as toxic to all living things as it is to the human body. If more than 10 µg/L of arsenic is present in the water, it creates a lethal effect for all living things in the water [6].

Copper is frequently used in many types of cables, coatings, pesticides, oil refineries as a nutrient additive, and in areas such as pyrotechnics. Ceruloplasmin is found in the structure of many enzymes such as SOD, cytochrome c oxide. Overexposure causes vomiting, abdominal pain, nausea, and liver failure. It causes menkes disease and Wilson's disease, which is a loss of pigment in the hair [7-9].

Cobalt is a relatively rare element of the Earth's crust, being one of the elements that are used abundantly in industry for different purposes [10]. Cobalt, B12, necessary to protect human health, is an essential and useful qualifier because it is part of the vitamin [11]. However, when excessive amounts of cobalt are taken into the body, it is known to adversely affect human health. It is stated that a worker in the cobalt industry suffers from asthma and skin ailments by constantly breathing air containing cobalt compounds [12].

Nickel is a silver white shiny and corrosion resistant metal. It is used in the construction of instruments used in laboratories due to its resistance to chemical substances. It is used in the construction of instruments used in laboratories due to its resistance to chemicals. Another important application of nickel is that it is a catalyst in many organic reactions [13]. Epidemiological studies in humans suggest that water-soluble nickel compounds are important in the formation of liver and nasal cancers exiled [14].

Cadmium is used in many industrial areas such as metal, electrical-electronics, automotive, and space technology [15]. The international cancer research agency has proved that cadmium is a carcinogenic agent in patients with lung, prostate and kidney cancer. [16].

Chromium is frequently used in leather industry, paint, ceramic and glass industry. Chromium is found in natural waters as +3 valued. Cr(VI) is very harmful compared to Cr(III) ion because it easily enters the cell membrane and damages it. Cr (VI) shows mutagenic effect with carcinogenic effect. Blood sugar and cholesterol level in people with chromium deficiency deteriorate [17].

Manganese is used in many areas such as firework making, cleaning products, glass and fuel industry [18]. There is no carcinogenic effect of manganese in the structure of many intracellular enzymes [19]. Excessive intake of manganese results in decreased testosterone levels, muscle weakness and lethargy [20]. Lead is used in many areas of the industry such as automotive, battery, electrical and electronics. Excessive lead intake has been shown to cause lower IQ levels, cancer and central nervous system in humans [21].

In drinking water, heavy metals are present in ppm (mg / L) and ppb (ng / mg) concentrations. It is quite important to know their concentration in drinking water. Table 1 also shows the heavy metal limit concentration in drinking water by WHO, EPA and TSE [22].

Table 1. Some acceptable heavy metal concentrations in drinking water by the WHO, EPA and TSE

Heavy metals	WHO (ng/ml)	EPA (ng/ml)	TSE (ng/ml)
As	10	10	10
Cu	20	20	20
Co	10	10	10
Ni	20	50	50
Cd	5	5	5
Cr	20	20	20
Mn	100	100	100
Pb	10	10	10

The aim of this study is to examine the levels of heavy metals in the surface waters of Siirt region seasonally in accordance with the literature information given above**.**

2. Material and Methods

2.1. Siirt region and surface waters

Siirt province is located in the southeast of our country, northeast of the Southeastern Anatolia region and south foothills of the Southeastern Taurus Mountains, and between longitudes 41-42 and latitudes 37-38. The center of the province was established on the slopes of Seven Hills between the Botan and Rashan rivers, which are tributaries of the Tigris River, and today it has started to spread into the plain. collection areas of the Tigris River. In the table (Table 2) below, you can find detailed information about surface waters in Siirt region [23].

Table 2. Gives information about the surface waters of Siirt region [23].

Surface Waters	Total Length Km	Length Within Provincial Boundarie Km	Flow rate M^3/sn
Bitlis River	108,8	56,3	18,5
Botan River	217,5	99	128,6
Kezer River	105	40	19,5
Zarova River	93,8	70	-

2.2. Climate of Siirt Region

The continental climate prevails in Siirt province. Summers are hot and dry, winters are cold and rainy. The north and east of the province gets colder in winter and cooler in summer. The average annual rainfall is 757 mm. In terms of forest presence, Siirt is one of the poorest provinces of Turkey. In some parts of the highlands, rickety shrub and oak communities are encountered. The natural vegetation of the province generally consists of steppe plants. The table (Table 3) below shows the average number of rainy days of the Siirt region by month [24].

Table 3. Average rainfall of Siirt region (Measurement period: 1939-2018) [24].

Siirt Station no:17210	Average Number of Rainy Days
January	12,4
February	12,0
March	14,0
Aprıl	13,1
May	10,3
June	3,3
July	0,6
August	0,6
September	1,6
October	7,2
November	9,0
December	11,5

When the changes in the average number of rainy days in the region studied are examined, it is seen that the rainy months are in January, February, March and April, while the driest months are June, July and August.

2.3. Collecting Surface Water Samples

Surface water samples were collected from the predetermined locations in March and July in 50 ml propylene containers. The pH of these samples was adjusted to 2 with HNO3 with a concentration of 67% and then the covers were closed and sent to the central research laboratory of Yıldız Technical

University. Samples brought to the laboratory are made of polyester membrane filters with a pore size of 0.45 µm. After passing, it was stored at +4 ºC until analysis time.

2.4. Device and Performance Values Used

In the analysis, agilent technologies were used as ICP-MS device and 7700 series as the model. Thermo scientific TKA smart pure was used as a pure water device. Standard solutions and chemicals prepared as main stock and decoction are of analytical purity. In the table (Table 4) below, performance information of the device we use in this research is given.

Table 4. Device and Performance Values Used

Device operating conditions		Unit
RF Power	1550	W
Carrier Gas (Argon)	1,08	L/min
Nebulizer Pump	0,1	rps
S/C Temp	2	℃
Plasma Gas	15	L/min

3. Results and Discussion

Turkey has a total area of 783562 km2. Although Turkey is a country surrounded on three sides by water, it is not a rich country in terms of fresh water presence. Turkey is in a climate zone of temperate, semi-arid and extreme temperatures. The average annual rainfall in Turkey is approximately 643 mm, below the world average (800 mm). The surface water potential of Turkey is 193 km3. In the light of this information, physical, chemical and biological monitoring of the surface waters within the borders of Turkey is of great importance. While evaluating the analytical performance of the device used for this follow-up, the values stated in the table (Table 5) below are taken into consideration.

Table 5. System analytic performance values

System analytic performance values			
	LOD, ng/mL	LOQ, ng/mL	%RDS
Cr	0,042	0,141	1,6
Mn	0,044	0,150	3,33
Co	0,021	0,069	5,21
Ni	0,230	0,750	1,89
Cu	0,051	0,171	2,84
As	0,032	0,105	4,09
Pb	0,009	0,288	4,73
Cd	0,006	0,019	2,96
Precision			
Mass	7	89	205
Range	1,00E+04	2,00E+04	2,00E+04
Count	6414,29	25850,46	13362,2
RSD%	3,8	3,4	3,8
Integration Time	0.100 sec		
Sampling Period	0.311 sec		
Oxide	156/140	1,51%	
Doubly Charged	70/140	1,51%	

Table 6. Results from Locations (ng/ml)

	As	Cu	Co	Ni	Cd	Cr	Mn	Pb
WHO	10	20	10	20	5	20	100	10
EPA	10	20	10	50	5	20	100	10
TSE	10	20	10	50	5	20	100	10
Botan (R)	1,4±0,06	0,34±0,001	ND	<0,23	ND	0,29±0,01	ND	ND
Botan (D)	1,75±0,07	0,1±0,01	ND	1,02±0,02	ND	0,44±0,01	ND	ND
Bitlis (R)	0,043±0,02	ND	ND	1,6±0,03	ND	1,83±0,02	ND	ND
Bitlis (D)	0,32±0,01	ND	ND	0,44±0,01	ND	0,75±0,01	0,25±0,01	ND
Zarova (R)	0,19±0,01	ND	ND	3,69±0,07	ND	0,64±0,01	ND	ND
Zarova (D)	0,23±0,01	ND	ND	ND	ND	0,48±0,01	0,11±0,01	ND
Başur (R)	0,41±0,02	0,18±0,01	ND	4,03±0,01	ND	1,85±0,02	0,15±0,01	ND
Başur (D)	0,38±0,02	0,12±0,01	ND	1,63±0,03	ND	0,87±0,01	0,17±0,01	ND
Kezer (R)	0,3±0,01	0,2±0,01	ND	ND	ND	1,12±0,02	ND	ND
Kezer (D)	0,37±0,02	ND	ND	ND	ND	0,6±0,01	0,17±0,01	ND

ND: Detection Limit Below, R: Rainy, D: Dry

Industrial activities, rapid urbanization, agricultural activities, uncontrolled wastes, spills, anthropogenic sources, accidents and environmental disasters are heavy metal sources. When the table (Table 6) above is examined, this study shows that the amounts of Co, Pb and Cd elements in the surface waters in Siirt region are below the device's determination limit. The quantities of other elements (Cr, Mn, Ni, Cu, As) are below the values determined by the WHO, EPA and TSE for drinking water. When the changes in the quantities of the elements in the surface waters as seasonal (rainy and arid) are examined, it is understood that there is no significant difference.

4. Conclusion and Recommendations

As a result of our study, it was observed that the amounts of heavy metals (As, Cu, Co, Ni, Cd, Cr, Mn, Pb) in the surface waters of Siirt region did not change significantly seasonally and were below the levels determined by WHO, EPA, and TSE. Our country's fresh water resources are limited. Therefore, it is important to monitor heavy metal levels in our surface waters and to protect these watersheds.

Author's Contributions:

All contribution belongs to myself in the article.

Statement of Conflicts of Interest:

There is no conflict of interest among the authors.

Statement of Research and Publication Ethics:

The authors declare that this study complies with Research and Publication Ethics.

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