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Evaluation of some Heavy Metals in Water Sulaimanih Governorate \ Kurdistan Region- Iraq

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ABSTRACT

Due to the significant increase in the number of cars and oil tankers after extracting it from multiple places in Sulaymaniyah Governorate, in addition to the great civilizational and architectural development witnessed by the governorate in recent years, which increases the sources of pollution, this study was actually conducted in four districts in Sulaymaniyah Governorate to estimate the concentrations of heavy metals, iron. (Fe), nickel (Ni), cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu) and zinc (Zn) in water (Darbandikhan, Khormal, Rania and Bakura Jaw). Samples were collected monthly from April to September 2016. , And by three replicates for each site. Plant samples were prepared and digested with appropriate acids to detect the concentrations of these minerals and using a Flame Absorption Spectrophotometer (FAAS). The results of the study showed that all the water in the sites is basic. The pH values ranged from (7.13 - 8.4), while the water temperature ranged between (17.6 - 24.3) degrees Celsius. The results also showed spatial and temporal differences in all the characteristics of the studied water and heavy metals. Heavy metals did not exceed the Iraqi limits for the quality of drinking water (2001) and the World Health Organization (2011) except for the element nickel, which recorded values that exceeded the permissible limits for each of the sites of Bakr Joe and Rana. The results of the current study recorded values lower than the detection limit for both cadmium and chromium in all the waters of the study sites. The seven heavy metals under study were recorded at different concentrations, as iron recorded the highest values in all study sites, and they were arranged in descending order as follows: Fe → Zn → Ni → Cu → Pb ← Cd → Cr.

Keywords: Heavy Metals, Water pollution, Kurdistan Region- Iraq.

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INTRODUCTION

Water is one of the main natural sources of human life and it is important for economic and social reasons. Water has a variety of purposes including drinking, agriculture, industry and energy production. [(1)] Agricultural and wastewater contain high levels of heavy metals that are often discharged into the environment. Where some heavy metals such as lead may also enter the atmosphere due to traffic pollution and industrial activities, which can be deposited in the surrounding sites and then enter the water with runoff. [(2)] Water has the ability to purify itself from the impurities attached to it and with the help of environmental factors, this is if the impurities are within the ability of the source to tolerate and treat them , and because of the increase in the volumes and concentrations of the flows, it becomes difficult for the water to purify itself by itself . [(3)] Note that the different uses of human societies made the amount of pollutants released into rivers in a steady increase . [(4)] The availability of water resources in countries is a major factor for development, so it is necessary to protect it from pollution problems and manage its uses [(5)] Approximately 20% of the world's population lacks safe drinking water and nearly half of the world's population lack proper sanitation , This problem suffers from many developing countries, which discard an estimated 5% of untreated wastewater in urban areas directly into Surface water. Iraq is one of nine countries in the Middle East that does not have enough fresh water. [(6)] Water bodies are affected because they receive water from sewage (point source), traffic drainage and runoff (non-point source). [(7)] The unscientific disposal of wastewater has caused enormous environmental problems not only for the aquatic environment but also for humans all over the world. This problem started a long time ago, but it intensified over the past few decades, and now the situation is worrying in Iraq. [(8)] The previous information shows the extent of the environmental risks of heavy metals on all life forms, and given the lack of information about the levels of heavy metals in Sulaymaniyah Governorate, especially after the urban, demographic and industrial development witnessed by the Kurdistan Region of Iraq. This study was conducted with the aim of achieving the following objectives: Study the concentration levels of seven minerals Heavy (iron, nickel, cadmium, chromium, lead, copper and zinc) in the waters of four different locations. In addition to making some physical measurements such as temperature and pH, and knowing the extent of their impact on the availability of heavy metals.[(9)]

MATERIALS AND METHODS

Sample Collection

Water samples were collected monthly from April to September 2016, with three replications from four different sites. Water samples were collected in the early morning between 8 am and 12 noon, using pre-sterilized polyethylene bottles. The bottles were washed several times with site water, then samples were taken and 1% nitric acid was added to them . [(10)]

Field Measurement

Water Temperature

The temperature was measured directly in the field by using a 0-100 ° C mercury thermometer, where the

thermometer was immersed in a depth of 10-15 cm for 5 minutes.

PH of Hydrogen Ion Concentration

The pH of the water was measured using a Portable PH field pH meter. Meter (HANNA) . [11]

Laboratory Analysis

Digestion of Water Samples for Heavy Metal Analysis

The water samples will be digested before the analysis according to. [12] In order to determine heavy metals, we take 500 ml of the water sample and place it in a 1000 ml glass baker, then add 5 ml of concentrated HNO3 to every 100 ml of the samples and boil slowly on a hot plate. Hot plate to continue evaporation until the final size of the sample reaches 15-20 ml, and we add several drops of concentrated HNO3 until the digestion is complete and the color of the bright or bright (clear solution) appears. We complete the volume to 50 ml of distilled water.

RESULTS & DISCUSSION

Physical properties of water

1- Temperature

Temperature is one of the most familiar environmental factors to have profound effects on life. It is an easily measurable factor that is almost universal in impact and often constrains the growth and distribution of plants and organisms. [13] The temperature of the water differed at the sites and during the sampling periods. As in, the highest value was recorded at 24.3 m in Darbandikhan in August. The lowest value of 17.6 m was recorded at the Roller Go site in April. As the fluctuation in water temperature depends on the season and geographical location .[14] It was mentioned . [15] that the source of water heat in most bodies of water is solar radiation as it accumulates directly by absorption and in some circumstances the heat becomes available by condensing the water vapor near the surface. It was noted from the statistical analysis that there is a significant difference between the study sites and with a probability (0.01), where the highest recorded rate of water temperature in Khormal site was 22.88 ° C, except for the site Khormal and Darbandikhan, so there was no significant difference in the water temperature, and this may be due to the convergence Both sites are under the influence of the same climate, meaning that the sun's rays are the reason that controls the water temperatures in the two sites. As for the temporal differences, it has been proven that there is a significant difference between the months of the study, because the water temperature tends to match the air temperature, as the highest average of water temperature was recorded at 22.5 ° C in the month of July and the lowest average temperature was 19.1 ° C in the month of April . The temperatures recorded in the study sites indicate that there is no thermal pollution in the water, as the temperature ranges are within the global permissible limits (8.5-34) m .

Table (1) ANOVA table of of water temperature

Tests of Between-Subjects Effects

Dependent Variable: Temp

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	330.833[a]	23	14.384	33.408	.000
Intercept	32004.500	1	32004.500	74333.032	.000
Sites	208.722	3	69.574	161.591	.000
Months	104.333	5	20.867	48.465	.000
Sites * Months	17.778	15	1.185	2.753	.004
Error	20.667	48	.431		
Total	32356.000	72			
Corrected Total	351.500	71			

a. R Squared = .941 (Adjusted R Squared = .913)

2. PH of water

The pH value is a result of the interaction of many factors, the most important of which are water temperature, the rate of consumption or production of CO2 by photosynthesis or respiration and decomposition of organic matter, as well as the alkalinity and acidity of . In this study, the pH values of water differed from 7.13 - 8.4, with the average total value being (7.71). The highest value was recorded on the Rania site in May, while the lowest value was recorded on the Khormal site in August. The pH results showed that the water in the study areas was basic, as all the values were more than 7 for all sites, which was expected from the pH value of the Iraqi internal waters, including Kurdistan, to be close to 8.0 due to the geological formation, which consists mainly of carbonates and bicarbonate , and Wissam thamer. The pH values during this study were within the natural limits of Iraq and the World Health Organization (WHO), and this is consistent with what was stated in the study [3] when they studied Darbandikhan Lake. The results of the statistical analysis showed significant differences between the monthly rates of the pH number, as the highest rates were recorded in May, reaching 7.96, while the lowest rates were recorded in August, reaching 7.50. While the spatial statistical differences showed that there is a significant difference between the study sites, as shown in. With the exception of the Darbandikhan site and Bikra Jaw, there were no significant differences, as the highest rate was recorded at the Rania site, which was 8.28, while the lowest pH rate was recorded at 7.43 in Khormal site. The location of Rania, thus increasing the amount of dust falling in the water due to the air and movement of cars, which leads to an increase in the pH value.

Table (2) ANOVA table of of PH water

Tests of Between-Subjects Effects

Dependent Variable: pH

Source	Type III Sum of Squares	df	Mean Square	F	Sig.

Sites	8.084	3	2.695	225.593	.000
Months	2.234	5	.447	37.407	.000
Sites * Months	1.195	15	.080	6.672	.000
Error	.573	48	.012		
Total	4301.010	72			

As for the spatial differences, the results of the statistical analysis showed significant spatial differences between all the study sites, as the Bakara Joe site recorded the highest rate of total dissolved solids and reached 370.27 mg / liter, while the site Rania recorded the lowest rate of 182.66 mg / liter. The reason for the high values of dissolved solids in the Bakara Joe site may be due to the water source in the area, as the water sources at the site can be seen from the spread springs and therefore the groundwater is considered to be water of high salinity. In addition, the Bakara Jaw area is an industrial area that is exposed to great pollution due to waste and factory waste.

Heavy metals in water

Iron

It is the most abundant mineral in the earth's crust and is found in natural fresh water at levels ranging from 0.5 to 50 mg / liter, and iron may be present in drinking water as a result of the use of coagulants or pipe erosion during water distribution , Although it is present in drinking water, it rarely exceeds 10 mg / liter, as iron does not pose a threat to human health if it is within the normal levels estimated at 0.3 mg / liter. The results obtained showed that the maximum iron value recorded in August at the Rania site was 0.074 mg / liter, while the minimum iron value was recorded in April at Khormal site and it was 0.014 mg / liter Statistical analysis of the data showed that there were some significant differences between the months of the study at (P <0.05) and significant differences between all sites.

The highest rates of iron were recorded in the hot months, as it reached the highest rates in August and September of 0.05 mg / liter compared to the lowest rates recorded in April and May, which amounted to 0.025 mg / liter. The reason for this is that temperatures affect the rates of photosynthesis in plants and the solubility of oxygen in Water, and thus with higher temperatures, the growth activity of plants decreases and they may die, leaving behind a substance that requires oxygen to decompose. This is in agreement with [4] The recorded values of iron concentrations in the water of the study areas were less than the maximum permissible limit for drinking water by the World Health Organization (2006) and the Iraqi standards of 0.3 mg / liter.

Table (3) ANOVA table of Fe concentration in water

Tests of Between-Subjects Effects

Dependent Variable: Fe

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.015[a]	23	.001	34.133	.000
Intercept	.100	1	.100	5262.897	.000
Sites	.005	3	.002	86.312	.000
Montes	.008	5	.002	86.357	.000
Sites * Montes	.002	15	.000	6.290	.000
Error	.001	48	1.904E-5		
Total	.116	72			
Corrected Total	.016	71			

a. R Squared = .942 (Adjusted R Squared = .915)

Nickel (Ni)

Nickel is naturally present in water, and is released into the atmosphere from natural sources (such as dust, plant forest fires, and volcanic eruptions) or from human activities (such as mining, smelting, manufacturing of stainless steel and other nickel-containing alloys, fuel combustion, and waste incineration , Nickel is an essential mineral for most animals and plants, and thus symptoms of deficiency or toxicity can occur when too little or too much nickel is ingested, as some researchers reported that an increase in the level of nickel to more than 5 parts per million in drinking water leads to cancer in different parts. From the human body , The nickel values ranged between 0.001 mg / L at the Darbandikhan site in the months of April and May as a minimum, and 0.08 mg / l at the Karawat site during the month of July as a maximum. The results of the statistical analysis showed that there are significant differences between the study sites, except for the two sites of Khormal and Darbandikhan, and at a probability degree (P <0.05). 0.0055 mg / L. The reason for the high nickel values in early Joe is explained by the exposure of this region to various types of pollution, as it is a densely populated industrial area, in addition to atmospheric precipitation, animal waste and the abundance of agricultural fertilizers. As for the temporal differences, the results of the statistical analysis recorded significant differences between the months of the study (P <0.05), as the highest rate was recorded in August and was 0.044 mg / liter, and the lowest rate was 0.013 mg / liter in the month of May, as we note the highest rates recorded in The hot months may be attributed to the evaporation of water, which leads to an increase in the concentration of minerals, as well as the precipitation that has reduced the concentrations of heavy metals.

Table (4) ANOVA table of Ni concentration in water

Tests of Between-Subjects Effects

Dependent Variable: Ni

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.065[a]	23	.003	271.850	.000
Intercept	.058	1	.058	5559.603	.000
Sites	.045	3	.015	1428.489	.000
Montes	.011	5	.002	212.864	.000
Sites * Montes	.009	15	.001	60.185	.000
Error	.000	48	1.041E-5		
Total	.124	72			
Corrected Total	.066	71			

a. R Squared = .992 (Adjusted R Squared = .989)

Lead

It is a highly toxic heavy metal that not only accumulates in individuals, but also has the ability to affect the entire food chain and disrupt the health system of humans, animals and plants , Lead is found in most types of rocks and is released during chemical weathering of minerals. Its quantities are low in ground and surface waters due to the insolubility of lead , Among the most important sources of lead in the water system is runoff and urban drainage, such as sewage treatment plants and industrial facilities, in addition to lead-containing paint, batteries and lead pipes used in water distribution , The highest value of lead was 0.02 mg / L at the Rania site in August, while the lowest value was below the detection limit of 0,000 mg / L at the Darbandikhan site during the months of April, May and June. The results of the statistical analysis showed that there are significant temporal and spatial differences between all study sites, and with a probability of P <0.05, the highest rate of lead concentrations was recorded at the Rania site and reached 0.013 mg / liter, while the lowest rate was recorded at the Bakir Joe site, which was 0.0001 mg / liter. The reason for the high values of lead in the Rania site may be attributed to the pollution that this area is exposed to, as it is a commercial exchange area between Sulaymaniyah and Iran, as well as the large number of oil wells and filtration stations. Large lead due to the combustion of leaded gasoline from cars. [5] stated when studying that one of the causes of pollution of Sulaymaniyah water and air is the frequent traffic of gasoline-powered vehicles. The month of August recorded the highest levels of lead concentrations, which reached 0.006 mg / liter, and the lowest rate recorded in April, which was 0.002 mg / liter. The reason for the high values of lead in the hot months and their decrease in the spring months is due to the absorption of dissolved chemicals and nutrients that occur during the growing season. Leading to a decrease in lead concentrations, while in the hot months, mineral concentrations increase due to evaporation and decomposition of organic matter after the death of many organisms, thus reducing productivity (live absorption) and thus a lack of oxygen. This is confirmed by several studies [7] While [5] explained one of the reasons for the high values of lead in water is its passage through agricultural lands, in which various chemicals containing lead are used in the production of agricultural crops.

Table (5) ANOVA table of Pb concentration in water

Tests of Between-Subjects Effects

Dependent Variable: Pb

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.003[a]	23	.000	387.218	.000
Intercept	.001	1	.001	4703.100	.000
Sites	.002	3	.001	2327.582	.000
Months	.000	5	5.314E-5	168.441	.000
Sites * Months	.000	15	2.274E-5	72.071	.000
Error	1.514E-5	48	3.155E-7		
Total	.004	72			
Corrected Total	.003	71			

a. R Squared = .995 (Adjusted R Squared = .992)

Copper

Copper is an essential micronutrient necessary for the growth of both plants and animals, but it is toxic even in low concentrations of aquatic organisms and high doses of copper can cause anemia, liver and kidney damage, and intestinal irritation [6] The results showed that the highest value of copper was 0.056 mg / l in the Rania site during the month of August, while in the Bakara Goh site in May the lowest value was 0.0001 mg / liter, and the average value of copper during the study period was 0.011 mg / liter. Agricultural activities may add large amounts of copper as fertilizers containing copper such as TSP contain 32 ppm, MAP contains 32 ppm and NPK contains 14 ppm , The results of the statistical analysis showed that there were no significant differences in the copper value between the study sites, with the exception of the Rania site, which recorded a significant difference with all the study sites, as it recorded the highest average copper value, reaching 0.039 mg / liter. The reason for the high copper values in Rania waters may be explained by the high alkaline pH values, as the Rania site recorded the highest pH value of 8.4, and this was confirmed by the positive correlation relationship between copper and the pH (r = 0> 000), which is based on the study [9] when studying Halabja water. As for the results of the temporal statistical analysis, they showed significant differences

between months and with a probability of P <0.05, as the highest average for copper values was recorded in August, and it was 0.018 mg / liter, while the lowest average for copper values was recorded in April, which was 0.002 mg / liter. The results indicated that the copper concentrations in the water and for all sites were within the permissible limits for drinking water and according to the Iraqi standards [6] and the World Health Organization (WHO, 2006) and confirmed that the water is considered contaminated if its concentration exceeds 1 mg / liter.

Table (6) ANOVA table of Cu concentration in water

Tests of Between-Subjects Effects

Dependent Variable: Cu

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.029[a]	23	.001	129.453	.000
Intercept	.010	1	.010	988.568	.000
Sites	.018	3	.006	635.867	.000
Months	.003	5	.001	64.763	.000
Sites * Months	.007	15	.000	49.734	.000
Error	.000	48	9.625E-6		
Total	.039	72			
Corrected Total	.029	71			

a. R Squared = .984 (Adjusted R Squared = .977)

Zinc

It is the fourth mineral in the world in terms of annual consumption, after iron, aluminum and copper , Zinc is an essential element found in drinking water in the form of salts or organic compounds. Zinc concentrations in tap water can be much higher than in surface water and groundwater due to the dissolution of zinc from pipes (WHO, 2011). Zinc is essential for living organisms and necessary for the enzymes needed to form red blood cells, and it is also necessary for plants because it participates in the biosynthesis of nucleic acids and polypeptides needed for plants. When zinc concentration exceeds a certain limit, it becomes toxic to humans, animals and plant life . The main sources of zinc in the environment are fertilizers, wastewater, mining, smelting and pesticides , The values of zinc in the water of the study areas ranged between 0.049 mg / liter at the Darbandikhan site during the month of August as a maximum, and 0.014 mg / liter at the site of Bakr Joe during the month of May, with an average of 0.028 mg / liter. The results of the statistical analysis showed that there are significant differences between all the study sites and with a probability of P <0.05, as the Darbandikhan site recorded the highest rate of 0.034 mg / liter and the lowest rate recorded at the Bakara Joe site, which was 0.021 mg / liter, and the reason for the higher concentrations in the Darbandikhan site may be explained Pollution that you are exposed to from sewage water from the Tangru River and its sources of zinc from soap, detergents and pesticides. The rates of April and May were significantly different with the rest of the study months and with a probability of p <0.05, as rates were recorded at 0.018 and 0.019 mg / liter, respectively, which are the lowest rates recorded among the rest of the study months and may explain the reason for the decrease in zinc values in these months to The mitigation process to which water is exposed due to the accumulation of rain [5] mentioned the reason for the increase in zinc values in the waters of several locations in Sulaymaniyah due to the use of plant fertilizers.

Table (7) ANOVA table of Cu concentration in water

Tests of Between-Subjects Effects

Dependent Variable: Zn

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.008[a]	23	.000	26.920	.000
Intercept	.060	1	.060	4944.816	.000
Sites	.003	3	.001	68.952	.000
Months	.004	5	.001	57.967	.000
Sites * Months	.001	15	9.977E-5	8.164	.000
Error	.001	48	1.222E-5		
Total	.069	72			
Corrected Total	.008	71			

a. R Squared = .928 (Adjusted R Squared = .894)

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