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Studying of some heavy metals levels in water samples from Kirkuk Irrigation project of Tuz Khurmatu District, Iraq

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ABSTRACT

The current study is conducted to estimate four heavy metals which are copper (Cu), lead (Pb), cadmium (Cd) and zinc (Zn) in the Kirkuk irrigation project which flows through Tuz Khurmatu district. The study samples are collected from the project water at a rate of one sample per month from November 2019 to August 2020 from three sites in Tuz Khurmatu district of Salah Al-Din Governorate. The first site is located before the project enters the district, and the second site is located within the boundaries of the district which is the meeting of the project with the Aqsu River and the site of dumping waste water in Tuz Khurmatu district. The third site is located outside the district. Generally, the results of the study show that the lead and cadmium metals are more concentrated than copper and zinc, the highest concentration of copper is 0.27 mg / L in the second site in March, and the lowest concentration is 0.008 mg / L in the first site in August. As for lead, the highest concentration is 0.21 mg / L in the second site in the month of March and the lowest concentration is 0.026 mg / L in the first site in the month of December. For cadmium, the highest concentration is 0.047 mg / L in the second site in June, and the lowest concentration is 0.001 mg / L in the first site in the month of December. The highest concentration for zinc is 0.098 mg / L in the second site in the month of March, and the lowest concentration is 0.022 mg / L in the third site in July. The results also show that there are great differences in varying seasons and locations.

Introduction

Heavy metals enter aquatic environments by specific and non-specific sources recording toxic concentrations in water bodies and their sediments[1]. Heavy metals pose a great danger to ecosystems because it is dose not decompose or break down causing toxic concentrations in the organisms' bodies and accumulate in the food network. This is considered a serious and critical problem affecting the health of ecosystems and their biota[2]. The study of the effect of heavy metals in the water and sediments of rivers takes a wide range day after day due to the importance of the water habitats and the impact of its pollution on human life and well-being. Large quantities of wastewater are produced in refining crude oil and producing electrical energy from black oil or natural gas causing toxic concentrations to be released from heavy metals leading to deterioration of water quality and wetlands[3]. The sediments Tigris River water inside

Turkish region record high concentrations of copper and nickel in the upper tributaries of the Turkish region due to copper mining factories and the production of its alloys[4], while the concentrations of the metals are less toxic in the river water and decrease continuously to reach the permissible concentrations before entering the Iraqi lands[5].

Aims of the Study: The aim of the study is to determine the concentration of heavy metals in the water of the Kirkuk irrigation project that meets the water of the Aqsu River and the waste water within the Tuz Khurmatu district, especially that the water of the project supply the Tuz Khurmatu district and its affiliated villages with drinking water and irrigates agricultural lands, in addition the Kifri district within the Sulaymaniyah governorate depends on the water of this project as a source for drinking water plant.

Description of study area: The concentrations of some heavy metals of the Kirkuk irrigation project

water are studied in Tuz Khurmatu district in three locations, and the distance between one site and another is estimated to be three kilometers. The first site is located in the north of the district in an agricultural area, in addition to the presence of block factories, and the second site is located to the west of the district, in which the water of the project meets the waters of Aqsu River which originates from the

heights of Sankaw in northern Iraq and passes through the center of Tuz Khurmatu district, in addition to its confluence with the waste water of the district. The third site is located south of the district in an agricultural area where gravel and sand quarries are abundant. The study area is defined by longitudes (44.26–44.58) to the east and two latitudes (34.30–35.10) in the north[6]. As shown in the figure below.



Fig. 1: study sites.

Materials and Methods

Estimation of some heavy metals in water samples:

The concentration of heavy metals were measured in this study according to [7]. A volume of 50 ml was taken from the sample in a beaker and the digestion process was performed by adding 5 ml of concentrated nitric acid, then placed over a hot plate and evaporated. Before dehydration, 5 ml of concentrated nitric acid is added to each sample, considering placing the Watch glass bottle above the beaker's mouth. Evaporation is repeated reaching to dryness and a colored precipitate is obtained. The precipitate was dissolved in 1-2 ml of nitric acid and the sides of the beaker as well as the watch bottle are washed with distilled water. The solution was heated and filtered and completed to 50 ml with distilled water and the solution becomes ready for measurement.

The metals Pb, Cd, Cu, Zn are measured using a UNICOM Model SP9 atomic absorption spectrophotometer, at the appropriate wavelengths for each metal (lead 232 nm, cadmium 248.3 nm, zinc 213.9 nm and copper 324.7 nm) after calibrating the device with standard solutions and adjusting the amount of oxidant (air) and fuel (acetylene) in units of (mg / L) and taking the standard curve for each metal.

Statistical Analysis: Using the statistical program SPSS 9th edition, the results are analyzed statistically according to the tests of the analysis of variance (ANOVA) and the calculation of the correlation coefficient.

Results and Discussion

Copper Cu: The results of the current study show that the copper metal values ranged from (0.008) mg / L in the first site during the month of August to (0.27) mg / L in the second site during the month of March. Noticed that copper ions record a greater concentration in the second site compared to the rest of the sites. This may be due to the drainage of most

of the water is thrown into the river, which is waste water that flows into the drainage system in the area, and which in turn flows into the Kirkuk irrigation project. In addition to the fact that the site is located near the main street linking Baghdad and Kirkuk which maybe increases the concentration of copper ions in that water. As for the presence of copper ions in other sites, it may be attributed to the fact that copper is used in agriculture, so it is abundant in water and soil[8]. The results of the statistical analysis for copper ions using the analysis of variance in Table (1) show the presence of significant localized differences (according to locations) at a significant level ($p \leq 0.01$) and the absence of significant temporal differences (according to months). When comparing the copper values recorded in the current study, we find it's were within the permissible limits (2 mg / L) according to limits of the World Health Organization for drinking water [9].

Table 1: monthly and local changes of copper ions (mg / L) in the study sites

Sites Months	St1	St2	St3	Months rates
Nov	0.012	0.23	0.015	0.086 a
December	0.010	0.20	0.014	0.075 a
Jan	0.022	0.18	0.020	0.074 a
Feb	0.011	0.22	0.021	0.084 a
March	0.010	0.27	0.015	0.098 a
April	0.012	0.19	0.018	0.073 a
May	0.016	0.26	0.010	0.095 a
June	0.009	0.013	0.011	0.011 a
July	0.017	0.020	0.014	0.017 a
August	0.008	0.010	0.009	0.009 a
Sites rates	0.012 b	0.159 a	0.014 b	

Notes: Similar letters mean that there are no significant differences between them

Lead Pb: The results of the current study show that the values of lead ions ranged from (0.026) mg / L in the first site during the month of December to (0.21) mg / L in the second site during the month of March. Noted from Table (2) that the values of lead ions are higher than the permissible limits of (0.01) mg / L

according to the World Health Organization for drinking water[10]. Noticed a clear increase in the concentration of lead ions in the spring and summer at the second site due to it located in an area in which abundant gravel and sand quarries and factories with machinery on the edge of the irrigation project. It is also located near the main road in the district of Tuz Khurmatu linking Baghdad and Kirkuk for the passage of large cars. Moreover, the high temperatures during this month increase evaporation and thus increasing the mineral concentration[11]. The high lead values in the first and third sites are may be due to the use of agricultural fertilizers that are washed with irrigation water into the project's water stream and their containment of high levels of lead [12] as well as the use of illegal fishing methods that use unpermitted explosive materials. The lead values are also high in the study by [13] on the Euphrates River, the study by [14] on the Euphrates River within the city of Ramady and the study by [8] in Eastern Ramadi. The results of the statistical analysis of lead ions using the analysis of variance in Table (2) show the presence of significant localized differences (according to sites) at a significant level ($p \leq 0.01$), and the presence of significant temporal differences (according to months) at a significant level ($p \leq 0.05$).

Table 2: monthly and local changes of lead ions (mg / L) in the study sites

Sites Months	St1	St2	St3	Months rates
Nov	0.035	0.060	0.042	0.0457 e
December	0.026	0.058	0.032	0.0387 e
Jan	0.029	0.110	0.071	0.0700 cde
Feb	0.041	0.054	0.064	0.0530 de
March	0.045	0.21	0.180	0.1450 a
April	0.030	0.122	0.090	0.0807 cd
May	0.061	0.200	0.133	0.1313 ab
June	0.057	0.178	0.112	0.1157 ab
July	0.072	0.143	0.098	0.1043 bc
August	0.065	0.159	0.114	0.1127 ab
Sites rates	0.046 c	0.129 a	0.093 b	

Cadmium Cd

Cadmium metal values in the current study ranged from (0.001) mg / L in the first site during the month of December to (0.047) mg / L in the second site during the month of June. The reason for the high level of cadmium in the second site may be due to the waste water of Tuz Khurmatu district, which is thrown into the water of the project without treatment. The sources of pollution come from detergents and paints that contain trace metals, including cadmium that accumulate in the agricultural soil and are exposed to the waterway during the rainy season[15]. As for the lowest values, they are recorded in the winter season, and the reason may be due to the amount of rain that reduces the concentrations of heavy metals[16]. The results of the statistical analysis of cadmium ions using the analysis of variance in Table (3) show the presence of localized significant differences (according to sites) at a significant level ($p \leq 0.05$), and the presence of

significant temporal differences (according to months) at significant level ($p \leq 0.01$). Cadmium values in the current study exceeded the permissible limits of (0.003) mg / L according to the World Health Organization for drinking water[9].

Table 3: monthly and local changes of Cadmium ions (mg / L) in the study sites

Sites Months	St1	St2	St3	Months rates
Nov	0.015	0.022	0.019	0.0187 e
December	0.001	0.020	0.013	0.0113 f
Jan	0.002	0.009	0.007	0.0060 g
Feb	0.017	0.028	0.021	0.0220 d
March	0.006	0.032	0.026	0.0213 d
April	0.035	0.039	0.037	0.0370ab
May	0.025	0.030	0.028	0.0277 c
June	0.040	0.047	0.036	0.0410 a
July	0.034	0.041	0.038	0.0377 b
August	0.01	0.02	0.018	0.0160 e
Sites rates	0.018 c	0.028 a	0.024 b	

Zinc Zn: Zinc metal values in the current study ranged from (0.022) mg / L in the third site during the month of July to (0.098) mg / L in the second site during the month of March. The increase in zinc values during the spring season is probably due to the types of sewage, especially the organic matter, which is a source of the zinc metal as indicated by[17]. The organic matter is the main source of the zinc metal, as well as the high water levels during the spring season works to wash away the fertilizers on agricultural lands adjacent to the water body or the riverbed which is confirmed by[18]. He showed that Iraqi fertilizers contain 406 ppm of zinc, as well as the impact of polluted water from the waste of asphalt factories near the second site or the waste water. The results of the current study were an approximate with the results of the study by [19] on the Tigris and the Lower Zab. The results of the statistical analysis of zinc ions using the analysis of variance in Table (4) show the presence of significant temporal differences (according to months) between the study sites at a significant level ($p \leq 0.01$), and the absence of significant local differences (according to the sites). When comparing the zinc metal values recorded in the current study, it's were within the permissible limits of (1mg / L) according to the Iraqi standard for drinking water for the year (1996), and international limits standard to (5 mg / L) [20].

Table 4: monthly and local changes of zinc ions (mg / L) in the study sites

Sites Months	St1	St2	St3	Months rates
Nov	0.075	0.092	0.083	0.0833 a
December	0.063	0.080	0.072	0.0717 b
Jan	0.067	0.059	0.080	0.0687 b
Feb	0.042	0.049	0.044	0.0450 cd
March	0.077	0.098	0.087	0.0873 a
April	0.053	0.059	0.046	0.0527 c
May	0.038	0.048	0.040	0.0420 d
June	0.032	0.037	0.034	0.0343 e
July	0.026	0.031	0.022	0.0263 f
August	0.030	0.038	0.034	0.0340 e
Sites rates	0.050 a	0.059 a	0.054 a	

Conclusions

1- The lead and cadmium metals in the current study recorded local and international unpermitted concentrations more than copper and zinc.

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2- The second site of the study recorded higher concentrations of heavy metals, higher than the other sites.

3- From the results of the current study that there are significant differences according to seasons and sites.

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دراسة مستويات بعض العناصر الثقيلة في عينات المياه من مشروع ري كركوك التابع لقضاء طوزخورماتو ، العراق

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الملخص

أجريت الدراسة الحالية لتقدير أربعة عناصر ثقيلة هي النحاس (Cu) ، الرصاص (Pb) ، الكاديوم (Cd) والزرنيخ (Zn) في مشروع ماء ري كركوك المار من قضاء طوزخورماتو، جمعت نماذج الدراسة من مياه المشروع بمعدل عينة واحدة شهرياً من شهر تشرين الثاني عام 2019 ولغاية شهر آب عام 2020 من ثلاثة مواقع في قضاء طوزخورماتو التابعة لمحافظة صلاح الدين، الموقع الأول يقع قبل دخول المشروع الى القضاء والموقع الثاني يقع ضمن حدود القضاء هو موقع النقاء المشروع مع نهر أقصو وموقع رمي مياه الصرف الصحي لقضاء طوزخورماتو أما الموقع الثالث يقع خارج القضاء. أوضحت نتائج الدراسة أن عنصري الرصاص والكاديوم أكثر تركيزاً من النحاس والزرنيخ بصورة عامة وكان أعلى تركيز لعنصر النحاس 0.27 ملغم /لتر في الموقع الثاني في شهر أذار وأدنى تركيز 0.008 ملغم /لتر في الموقع الأول في شهر آب أما الرصاص فكان أعلى تركيز له 0.21 ملغم /لتر في الموقع الثاني في شهر أذار أيضاً وأدنى تركيز 0.026 ملغم /لتر في الموقع الأول في شهر كانون الأول، أما الكاديوم فأعلى تركيز له كان 0.047 ملغم /لتر في الموقع الثاني في شهر حزيران وأدنى تركيز 0.001 ملغم /لتر في الموقع الأول في شهر كانون الأول، أما الزرنيخ فكان أعلى تركيز له 0.098 ملغم /لتر في الموقع الثاني في شهر أذار وأدنى تركيز كان 0.022 ملغم /لتر في الموقع الثالث في شهر تموز وتبين من النتائج وجود اختلافات كبيرة باختلاف الفصول والمواقع.